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Characterization of Stack Emissions from Municipal Refuse-to-Energy Systems

Battelle Columbus Labs., OH

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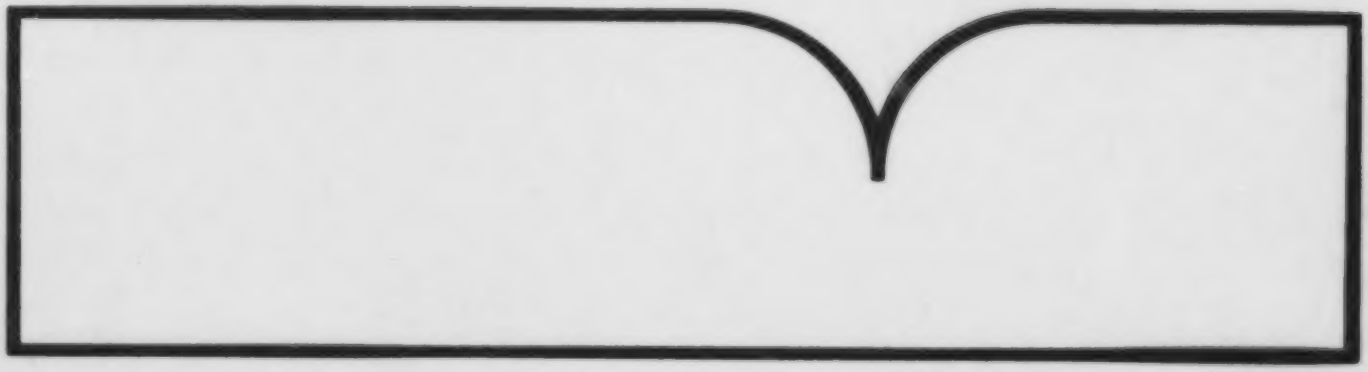

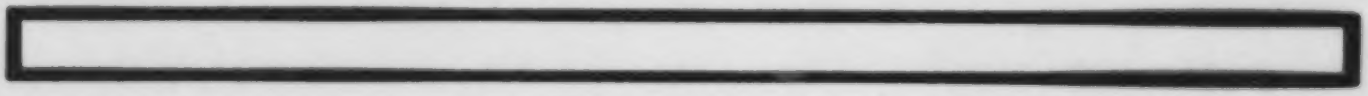

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CHARACTERIZATION OF STACK EMISSIONS FROM MUNICIPAL REFUSE-TO-ENERGY SYSTEMS

by

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The physical characterization included measurement of the mass concentration, and size distribution of the stack particulate matter. Inorganic chemical characterization of the stack emissions included determination of the elements, anions, and compounds present in the fly ash, measurement of gaseous HCl and HF emissions, and determination of volatile trace element levels. The characterization of organic materials in the stack emissions included specific measurements for polynuclear aromatic hydrocarbons (PAH), tetrachlorinated dibenzo-p-dioxins (TCDD) and dibenzofurans (TCDF), and aldehydes. Screening analyses were performed to provide tentative identification of organic compounds in the stack emissions.

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ABBREVIATIONS AND SYMBOLS

Abbreviations

TPD--tons per day
cm--centimeter
μm--micrometers
dscm--dry, standard cubic meters (20C, 760 mm Hg)
kg--kilogram
g--gram
mg--milligram (10^{-3}g)
μg--microgram (10^{-6}g)
ng--nanogram (10^{-9}g)
C--degrees Centigrade
amμ--atomic mass units
ev--electron volts
ms--milliseconds
hr--hour
ppm--parts per million
ppb--parts per billion

SECTION 1

INTRODUCTION

Vast quantities of municipal refuse are generated daily throughout the United States. In New York City alone, over 25,000 tons of refuse are generated each day. By the year 2000, refuse collections for New York City are projected to be about 35,000-40,000 tons/day.

Although incineration has been used for reduction of refuse volume in the past, the most common and economical method of disposal has been the use of landfills or open dumps. However, the availability and cost of convenient landfill sites and public acceptance makes this option less economically attractive as a future disposal method. A second important factor which will impact on future waste disposal practice is the increased emphasis on energy conservation. Municipal refuse represents an energy source which when burned can supply steam for heat and electricity production. Because of these land and energy conservation considerations, it is anticipated that there may be a significant increase in refuse-to-energy incineration of municipal refuse in the future.

An important issue which must be addressed in view of the expected proliferation of energy-to-refuse incineration systems is the potential release of hazardous pollutants into the environment from these facilities. The information base is limited and additional work is needed to develop emission data to answer the environmental questions, particularly in the case of newer refuse-to-energy incinerator systems.

The purpose of the research program described in this report was to characterize the physical and chemical composition of airborne emissions from municipal refuse-to-energy units. The study included a comprehensive set of physical and chemical measurements which identify and quantify the emissions of three refuse-to-energy units; a refuse-derived fuel, mass burning, and modular design. Thus, the emission data provides an important contribution to the data base available to assess the environmental impact of refuse-to-energy systems, to identify specific pollutants which may have adverse health and/or environmental effects, and to determine the need for process and/or control technology modifications to reduce pollutant emissions.

SECTION 2

CONCLUSIONS

This study provides a comprehensive set of physical and chemical characterization data to support assessment of the impact of minicipl refuse-to-energy system emissions on public health and the environment and to guide future similar studies. The data show wide variations in the composition and levels of various species in the stack emissions both among the various units studied and among repetitive measurements at the same unit. These variations may be due to influences from one or a combination of the following factors: unit type, unit design, refuse composition, or operating conditions. The scope of this study did not encompass the collection of data and measurement of the parameters required to evaluate the factors that influence refuse-to-energy system emissions. It is assumed that "normal" operating conditions prevailed during the emission measurements, however, the possibility that abnormal operating events occurred during test period and that these events influenced the emission characteristics, cannot be discounted. This possibility should be kept in mind in considering the following conclusions.

- The high concentration and the relatively large size particulate emissions indicates either inefficient operation of the electrostatic precipitators (ESP) on the RDF and MASS units or combustion conditions for which the ESP's were not designed.

- The particulate emissions from the three types of refuse-to-energy units are similar in inorganic chemical composition. The group of elements that are unique to municipal refuse incinerator emissions include; zinc, titanium, bromine, tin, antimony, cadmium, and lead. Inorganic compounds in the emissions are present primarily as chlorides and sulfates.

- The emissions from the municipal refuse-to-energy units varied greatly in organic chemical composition. This result is presumably due to design differences and variations in refuse feed composition and operating parameters of the units.

SECTION 3

RECOMMENDATIONS

This study has yielded a comprehensive data base to support environmental assessment of municipal refuse-to-energy systems and to identify areas that may require additional research. The most urgent need of future studies is to acquire the supporting data required to establish the incinerator operating conditions during emission measurement periods. This information would identify abnormal conditions and, in general, would permit the elucidation of the relationship between design and operating parameters and emission chracteristics.

Based on data obtained in this study, it appears that improvements in design and/or operation of municipal refuse-to-energy systems could be made to reduce stack emissions. In general, modifications e.g., in refuse preparation, combustion air feed, etc., that increase combustion efficiency should significantly reduce emission levels. Control devices should also be selected and/or operated to provide more efficient capture of particles from the emission stream. Future studies should adopt a parametric experimental design to clearly identify the design and operational variables that influence emission levels and to optimize conditions for emission reduction.

SECTION 4

EXPERIMENTAL PROCEDURES

The study involved a comprehensive set of measurements to characterize the physical and chemical composition of stack emissions from three refuse-to-energy units. A summary of the measurements that were performed and the sampling and analytical methods that were employed in the study is given in Table 1. The following sections provide descriptions of study sites and the procedures used to collect and analyze the emission samples.

SITE DESCRIPTIONS

Stack emission measurements were performed on three refuse-to-energy incineration units. A summary of the characteristics of the units is provided in Table 2. The sites included recently constructed units of three different designs; refuse-derived fuel (RDF), mass burning (MASS) and modular (MOD). All three units were fueled with solid municipal refuse, however, approximately 30 percent of the modular unit feed came from industrial sources. Refuse feed for the RDF unit was shredded and pneumatically and magnetically classified while the MASS and MOD units burned unclassified bulk refuse. The feed rate data given in the table are estimates for the period during which tests were conducted and do not necessarily represent the design capacity of the units.

At all sites, the emission measurements were performed by sampling from a duct or stack downstream of the control devices, if present. Operating conditions considered "normal" for each unit prevailed during the respective test periods. Detailed data were not available on the composition of the refuse feed nor the plant operating conditions during the test periods.

PHYSICAL CHARACTERIZATION OF EMISSIONS

Particulate Mass Concentration

The mass concentration of particulate material emitted from the refuse-to-energy units was determined using the equipment and procedure described in EPA Method 5[1]. EPA Methods 1, 2, and 3 (Fyrite Method)[2,3,4] were used in conjunction with Method 5 for selection of traverse points, measurement of gas velocity, and determination of combustion gases, respectively.

TABLE 1. SAMPLING AND ANALYTICAL METHODS USE FOR CHARACTERIZATION OF REFUSE-TO-ENERGY SYSTEM STACK EMISSIONS

Measurement	Sampling Method	Analytical Method
Particulate Mass	EPA Method 5	Gravimetric
Particle Size Distribution	Andersen In-Stack Impactor	Gravimetric
Elemental Composition of Flyash	Source Assessment Sampling System (SASS) (Cyclones/filter catch)	(1) Spark-source mass spectrometry (2) X-ray fluorescence (3) Combustion
Volatile Trace Elements	SASS (impingers loaded with ammonium persulfate/ silver nitrate solution	Atomic absorption
HCl/HF	Impinger train with 1N NaOH solution	Ion chromatography
Anions in flyash	SASS (Cyclones/filter catch)	Ion chromatography
Polyaromatic hydrocarbons (PAH)	SASS (Cyclones/filter/ XAD-2 catch)	Combined high resolution gas chromatography/ mass spectrometry (HRGC/MS)
Tetrachlorodibenzo-p-dioxins/tetrachlorodibenzo furans (TCDD/TCDF)	SASS (Cyclones/filter/ XAD-2 catch)	Combined high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS)
Aldehydes	Impinger train with dinitrophenyl hydrazine solution	High performance liquid chromatography (HPLC)/ fluorescence
Organic compound screening	SASS (Cyclones/filter/ XAD-2)	HRGC/MS - computer search/ spectra matching
Volatile organic compounds	Stainless steel cannister grab samples	Capillary column gas chromatography with FID and EC detection

TABLE 2. SUMMARY OF STUDY SITE CHARACTERISTICS

	Refuse-Derived Fuel Unit	Mass Burning Unit	Modular Unit
Site Code	RDF	MASS	MOD
Process characteristics	• shredding • air classification • magnetic separation • semi-suspension stoker-grate boiler	• mass burning • bulk refuse	• Consumat unit • bulk refuse
Feed	Municipal refuse	Municipal refuse	Municipal and commercial refuse
Estimated feed rate during study	600 TPD	125 TPD	50 TPD
Emission control	Electrostatic precipitator	Electrostatic precipitator	None
Stack gas temperature	230°C	270°C	255°C

Three Method 5 tests were performed to measure particulate mass concentrations in the stack emissions of each incinerator. Sampling was performed in a duct or stack after any existing emission controll devices.

All tests were performed by sampling for a total of 120 minutes at traverse points selected according to Method 1. Total sample volumes ranged from approximately 1.6 to 2.6 dscm. The Method 5 train operating conditions and the stack gas conditions prevalent during the tests are summarized in the Results and Discussion Section.

Particle Size Distribution

Particle size distribution of the stack emissions of each incinerator unit was determined with an Andersen cascade impactor. The Andersen impactor contains 9 jet plates which fractionate the particulate material into 8 size ranges based on aerodynamic particle diameter. The approximate cut-points of the size ranges were 0.5, 0.9, 1.5, 3, 5, 7, 10, and 16 μm. For sampling, the impactor was used in conjunction with an EPA Method 5 train. The impactor was mounted on the front of the probe and a goose-neck nozzle was used to extract sample from the stack gas stream. Sampling was performed isokinetically for 5 to 15 minute periods with the nozzle placed at a point of average velocity (P) in the gas stream. The impactor temperature during sampling was measured with a thermocouple imbedded in the impactor wall.

Glass fiber mats were used on the impactor stages to better retain the particles and to minimize particle bounce which would lead to erroneous distribution data. Prior to sampling, the glass fiber mats were desiccated for at least 24 hours and weighed. Weights of the mats after sample collection was performed in the same manner. A Mettler microbalance (1 μg sensitivity) was used to obtain all gravimetric data.

CHEMICAL CHARACTERIZATION OF EMISSIONS

Sampling

The samples used for chemical characterization of the incinerator emissions were obtained with a modified Source Asessment Sampling System (SASS). A diagram of the SASS train is shown in Figure 1. The SASS train modification consisted of replacement of the stainless steel module used to collect semivolatile organic compounds with glass counterparts. A glass condenser cooled with ice water from the impinger bath was used to cool the gas stream temperature to <20°C. Following the condenser were a glass trap containing 150 g of purified XAD-2 and a glass reservoir to collect the condensate water.

A description of the SASS equipment and operating procedures are presented in the SASS operation manual and an IERL/RTP Procedures Manual (5,6). Particulate material extracted from the stack was collected in a series of cyclones followed by a quartz fiber filter. Semivolatile organic compounds (approximate boiling point range of 100-300°C) were collected in the condenser and XAD-2 trap. Volatile trace elements (Hg, Se, As, Sb, etc.) were trapped

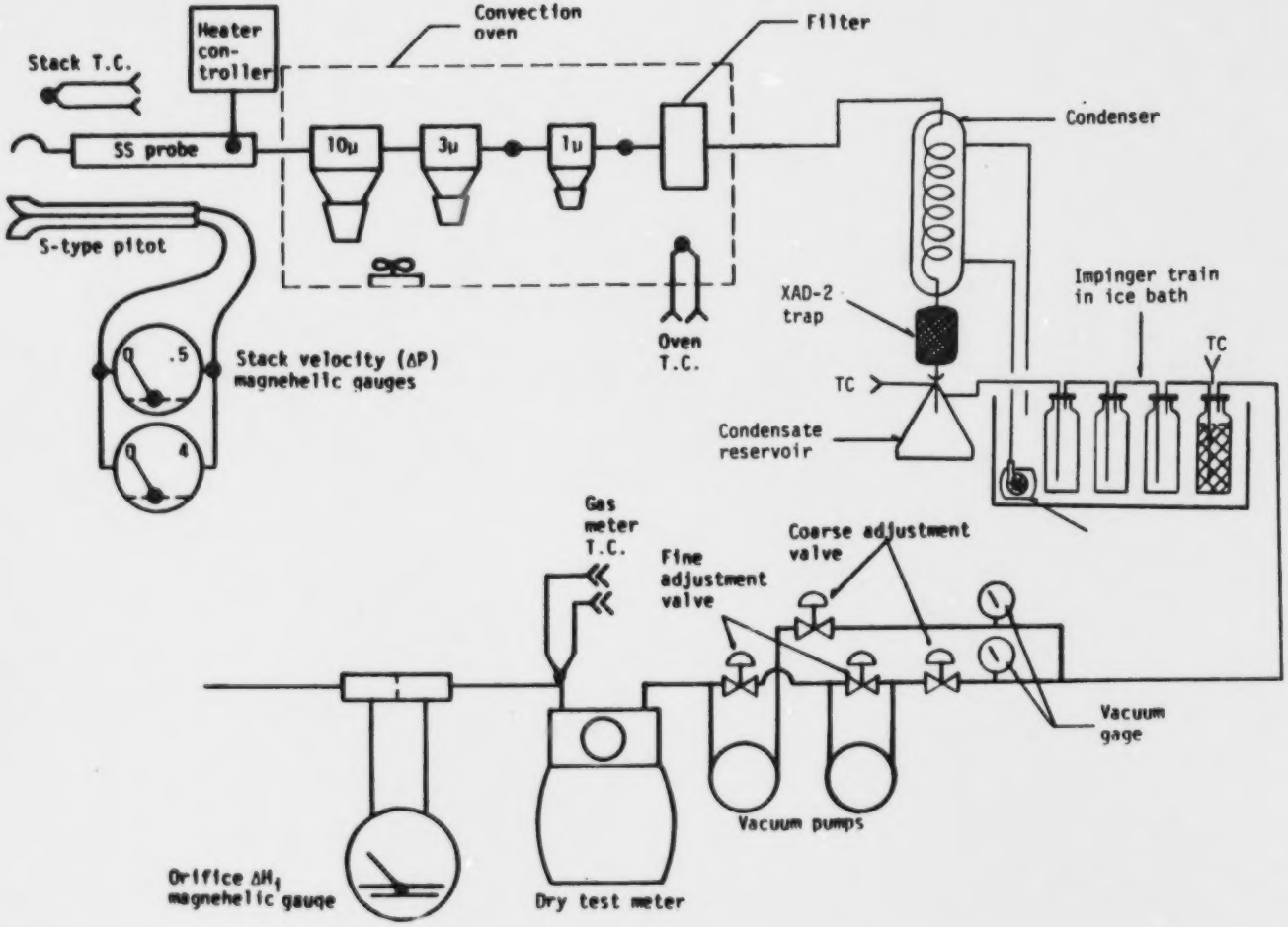

Figure 1. Diagram showing components of modified SASS train.

in the liquid impinger train which contains hydrogen peroxide in the first impinger and ammonium persulfate/silver nitrate in the two following impingers.

The particulate collection components of the sampling train were operated at approximately 204°C. The gas temperature through XAD-2 trap and the impinger train was maintained at <20°C.

Sampling of the emissions at each of the sites was performed in a duct or stack downstream from all control devices. The train was operated at a constant sampling rate at a single point in the duct or stack. Sampling times ranged from 120 to 180 minutes and total volume of gas sampled ranged from 11.3 to 17.1 dscm.

For the chemical characterization of the stack particulate material, aliquots of the combined, homogenized catch from the cylones and the filters were used. The organic analyses were performed on the combined extracts of the XAD-2 and the condensate water and the methylene chloride rinse of all the organic module components. Volatile trace elements were determined by

analysis of aliquots of the H_2O_2 and ammonium persulfate/silver nitrate impinger solutions.

The SASS train operating data for the test performed at each of the incinerators is provided in the Results and Discussion Section.

Inorganic Composition

Elemental Composition--

The elemental composition of stack particulate samples was determined by spark-source mass spectroscopy (SSMS), x-ray fluorescence spectroscopy (XRF), and combustion techniques. The procedure described in the IERL-RTP Procedures Manual (6) was used for the SSMS analyses. An AEI Model 702-R spark-source mass spectrometer was used for the work. The accuracy results obtained by SSMS are generally considered to be in the range of -50 to +100 percent. The XRF analyses were performed by the Source Emissions Branch, Environmental Sciences Research Laboratory, Research Triangle Park, North Carolina, using wave-length dispersive instrumentation. Carbon, hydrogen, and nitrogen were determined by combustion using a Perkin-Elmer Model 240 elemental analyzer system. Total sulfur was determined with a LECO Model IH-10S combustion/titration system.

Volatile trace elements in the stack emission that were collected in the SASS train impingers were determined by atomic absorption spectrometer (AAS) using a Perkin-Elmer Model 603 system. A flameless, UV technique (7) was used to determine mercury. Arsenic (As), selenium (Se), and antimony (Sb) were determined by hydride generation techniques described in the IERL-RTP Procedures Manual (6). Lead (Pb) was determined using a graphite furnace operated at the conditions given in the Perkin-Elmer Operating Manual (8). For all AAS determinations, samples of the ammonium persulfate/silver nitrate

impinger solutions were prepared by removal of the silver by precipitation as the chloride. For As, Se, and Sb analysis, organic materials in the solution were then destroyed by addition of sulfuric, nitric, and perchloric acids and heating until fuming occurred. The hydrogen peroxide in the impinger solutions was destroyed by addition of potassium permanganate prior to mercury determinations.

Anion Compositions--

The anionic composition of stack particulate samples was determined by ion chromatography (IC). Samples of the fly ash collected with the SASS train were prepared by leaching with distilled water. The leach solution was then analyzed using a Dionex Model 10 Ion Chromatograph using the procedures described by O'Dell, et al (9). The anions determined by IC were sulfate, nitrate, chloride, bromide, fluoride, and phosphate.

Solubility--

The solubility of the particulate emissions was determined by leaching a 1-gram sample with 100 ml of distilled water for about one hour. A magnetic stirrer was used to mix the solution during the leach period. The solution was maintained at room temperature (22^{o}C) and the pH was not controlled.

HCl/HF Measurements--

Hydrochloric acid and hydrofluoric acid in the stack emissions from the refuse-to-energy units were sampled with the type of impinger train used for EPA Method 6 (10). The acids were collected in 1 N sodium hydroxide contained in the first two impingers of the train. Sampling was performed for 30 to 45 minute periods and total sample volume ranged from 1.5 to 2.3 dscm.

The chloride and fluoride content of the impinger solutions were determined by ion chromatography using the procedure described by O'Dell, et al (9).

Determination of Inorganic Compounds by Infrared Analysis--

Analyses for inorganic compounds in the particulate emissions of the three refuse-to-energy units were performed by the Fourier Transform Infrared (FT-IR) techniques described by Jakobsen, Gendreau, et al (11,12,13). The samples from each unit used in the FT-IR analyses consisted of (a) the as-received stack particulate material, (b) the freeze-dried water soluble fraction of the stack particulates, and (c) the water insoluble fraction of the stack particulates. FT-IR spectra of each of these sample types (a, b, and c) were obtained both before heating (unbaked) and after heating for three hours at 200^{o}C (baked).

For the analysis, two to four milligrams of each type sample was ground, mixed with approximately 300 mg of potassium bromide and pressed into pellets. Smaller quantities of the MOD and water soluble fractions were required for analysis. Because of the carbon content, it was necessary to use larger quantities of the RDF and MASS samples for the analyses. Although elemental carbon does not have an infrared spectrum, it does cause both baseline and throughput problems because it is highly absorbent and causes scattering problems. Spectra of each of these pellets were obtained between 3600 and 400 cm^{-1} on a Digilab Fourier transform infrared (FT-IR) spectrometer at a resolution of 4 cm^{-1}.

Spectra of the water soluble samples, both baked and unbaked, were deconvoluted using a computer program developed by Doug Moffat of the National Research Council of Canada (14). This procedure is used for resolving a complex band into its components. The specific Fortran program used assumes a Lorentzian line shape and a band width chosen by the spectroscopist. The deconvolution procedure takes place in interferogram domain and in this case, a triangular apodization was used.

Spectra were compared to spectra of reference compounds both from the Battelle library of inorganic compound spectra and from Nyquist and Kagel (15). Identifications were made based on band for band matches as well as the occurrence of spectral changes due to changes in hydration state upon baking. Cation and anion compositional information obtained from the other analysis techniques was also considered in the compound identification procedure.

Organic Composition

PAH Measurements--

The procedure used for determination of polynuclear aromatic hydrocarbons (PAH) in the emission samples consisted of (a) extraction of the PAH compounds from the sample matrix, (b) liquid chromatographic cleanup of the extract, and (c) analysis and quantification by high resolution gas chromatography/mass spectrometry (HRGC/MS).

Sample Extraction and Cleanup--The particulate and XAD-2 samples were extracted with methylene chloride in a Soxhlet apparatus for at least 16 hours. The condensate water sample was extracted with methylene chloride for approximately 24 hours using a magnetic stirrer. Extracts of the XAD-2 and the condensate and the methylene chloride rinse of the organic module were combined. After extraction, the samples were concentrated to 1 milliliter in a Kuderna-Danish apparatus and spiked with internal standards. The internal standards used were 5 μg each of D_{10}-phenanthrene, D_{10}-pyrene, D_{12}-chrysene, and D_{12}-perylene. The extracts were then processed by silica gel chromatography to remove interfering species as described in EPA Method 610 (16).

Analysis by HRGC/MS--The analyses of the samples for PAH was performed by high resolution gas chromatography/mass spectrometry (HRGC/MS). The following HRGC/MS operating conditions were used:

70 ev electron impact ionization
Full scan spectra (40-400 amu) were collected
GC column - 30 meter SE-52 glass capillary
Carrier flow - 20 cm/sec helium
Temperature program - 70-270°C at 4 degrees C/minute.

A reverse search of the mass spectra was to identify the PAH compounds in the samples. Quantification of the PAH levels was performed by comparing the molecular ion current peak areas to that of the most closely related deuterated internal standard.

TCDD and TCDF Measurements--

Measurement of TCDD and TCDF levels in the stack emission samples involved three basic steps: (a) extraction of the TCDD and TCDF from the sample matrix; (b) sample clean-up to remove co-extracted interferences; and (c) analysis of TCDD and TCDF by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Several intermediate steps were required to reduce sample volume and to exchange the extract to a solvent suitable for subsequent operations.

Extraction Procedure--Soxhlet extraction procedures were used to extract the TCDD and TCDF from the particulate samples and the XAD-2 gas phase samples. TCDD and TCDF in the condensate water samples collected after passing through the XAD-2 was concentrated by liquid-liquid extraction. For determination of TCDD and TCDF in the gas phase of the stack emission, the XAD-2 and condensate water extracts and the methylene chloride rinse of the organic module were combined. Extracts of the particulate and gas phase sample extracts from selected tests were combined for analysis. Samples from at least one test at each site were analyzed separately to determine TCDD and TCDF distribution between the particulate and gaseous phases of the stack emissions.

For the extraction, the particulate samples were transferred into the extraction thimble and placed into the Soxhlet apparatus. The 2,3,7,8-TCDD-$^{13}C_{12}$ internal standard was added and the samples were extracted with methylene chloride. Teflon tape was used to seal the ground glass joints to minimize evaporative losses. Following the extraction, the methylene chloride was transferred to an Erlenmeyer flask using three 15 ml rinses of fresh methylene chloride. The methylene chloride was dried by slowly adding approximately 1 g of anhydrous sodium sulfate. The sodium sulfate was added slowly to prevent the formation of clumps which can entrap the TCDD and TCDF. The dried extract was then transferred to a Kuderna-Danish (K-D) apparatus using three 15 ml rinses of fresh methylene chloride and concentrated to approximately 5 ml volume. The extract was stored in a glass stoppered bottle at 0°C until processed through the acid/base and chromatographic clean-up steps.

The XAD-2 resin samples were Soxhlet-extracted using methylene chloride. The resin was transferred into a pre-extracted cellulose extraction thimble, spiked with 2 ng of 2,3,7,8-TCDD-$^{13}C_{12}$ and allowed to extract for at least 16 hours. The methylene chloride extract was dried with anhydrous sodium sulfate and concentrated in a K-D apparatus to a volume of approximately 5 ml following the same procedure as described for the particulate extracts.

The condensate water samples were extracted by liquid-liquid extraction using methylene chloride. The entire contents of each sample was transferred to a two-liter glass bottle and spiked with 2 ng of 2,3,7,8-TCDD-$^{13}C_{12}$. A Teflon-coated magnetic stirring bar was added and the sample was stirred for about 30 minutes. A 300 ml portion of methylene chloride was added and the stirring resumed for at least 24 hours. The methylene chloride extract was then transferred to an Erlenmeyer flask using three 50 ml rinses of fresh methylene chloride, dried with anhydrous sodium sulfate, and concentrated to 5 ml using the procedure described for the particulate extracts.

Sample Clean-Up Procedures--The methylene chloride extracts of the particulate and gas phase stack samples were treated to remove interferences using a series of liquid chromatography columns. The first column used to treat the extracts was a multilayered silica column which served to remove acidic, basic, and easily oxidized compounds. The column contained approximately 4 g of silica treated with sulfuric acid, 4 g of silica treated with sodium hydroxide, and 2 g of activated silica. The column was packed dry and pre-rinsed with 25 ml of hexane prior to use.

The sample extracts were transferred onto the silica column using three 5 ml rinses of hexane/benzene (50:50). The extract was eluted with 50 ml of hexane/benzene (50:50) and the total eluate (about 70 ml) was collected. The eluate was then concentrated nearly to dryness under a gentle stream of purified nitrogen and dissolved in about 5 ml of hexane.

The extract (in hexane) was transferred to a 5-g activated alumina clean-up column. The column was pre-rinsed with 25 ml hexane followed by the addition of the sample. The column was sequentially eluted with 25 ml portions of hexane, hexane/carbon tetrachloride (1:1), and hexane/methylene chloride (1:1). The hexane/methylene chloride fraction was collected and stored at 10°C until analyzed. Just prior to analysis, the hexane/methylene chloride solution was evaporated to dryness at ambient temperature using a stream of purified nitrogen. The residue was then dissolved in 20 µl of n-decane (accurately measured). Analysis for TCDD and TCDF was performed on a 2 µl aliquot of the n-decane solution.

HRGC/HRMS Analysis of TCDD and TCDF--The extracts were analyzed for TCDD and TCDF using combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS). A Carlo Erba Model 4160 gas chromatograph interfaced to a VG Model 7070H high resolution mass spectrometer was used for the analyses. Typical operating parameters were:

Mass Spectrometer	
Electron Impact Ionization	- 70 ev
Mass Resolution	- 10,000-12,000 (m/ m, 10% valley)
Source Temperature	- 200°C
Multiple Ion Detection Mode	- 25 ms dwell time, total cycle time 200 ms
Gas Chromatograph	
Column	- 30 meter DB5 or 60 meter SP2340 Fused Silica Column
Carrier Flow	- 30 cm/sec (helium)
Injector Temperature	- 275°C
Temperature Program	- 140°C for 3 minutes; linear increase to 275°C at 20°C/ minute and hold at 275°C for 10 minutes
Transfer Line	- 290°C

A VG Model 2035 Data System was used to control the multiple ion detection (MID) acquisition and to acquire the time-intensity data. Seven ion masses shown below were monitored.

318.9793	Reference Lock Mass (Perfluorokerosene)
303.9016	TCDF
305.8987	TCDF
319.8965	TCDD
321.8936	TCDD
331.9368	2,3,7,8-TCDD-$^{13}C_{12}$ internal standard
333.9338	2,3,7,8-TCDD-$^{13}C_{12}$ internal standard

The criteria for a positive identification were:

1. Correct chromatographic retention time within ± 2 seconds based on 2,3,7,8-TCDD-$^{13}C_{12}$ internal standard and external standards

2. Response at both m/z 304 and m/z 306 for TCDFs

3. Response at both m/z 320 and m/z 322 for TCDDs

4. Isotopic ratio correct for a tetrachloro compound ($0.77 \pm 10\%$)

5. Signal-to-noise ratio equal to or greater than 2.5 to 1.0.

The TCDD and TCDF were quantified by comparison of the responses (selected ion current profile peak areas), of the native TCDD/TCDF isomers with the response of the 2,3,7,8-TCDD-$^{13}C_{12}$ internal standard. Thus all reported TCDD/TCDF levels were corrected for the recovery efficiencies. A response factor of 1.0 relative to the internal standard was assumed for all TCDD and TCDF isomers.

The 2,3,7,8-TCDD standard solution used for calibration of the HRGC/HRMS system was prepared gravimetrically, i.e., dissolution of an accurately weighed quantity of the compound in an accurately measured volume of solution. The concentration of 2,3,7,8-TCDD$^{13}C_{12}$ internal standard solution used in the analyses was verified by comparison of standards prepared by the U.S. Environmental Protection Agency (R. Harless, HERL/RTP), University of Nebraska, McMaster University, and Monsanto.

The HRMS was tuned to a reference peak from perfluorokerosene (PFK) which was continuously monitored during analyses and the 2,3,7,8-TCDD peaks referenced to the PFK response.

After this study was conducted the U.S. EPA joined with the U.S. Department of Energy and the American Society of Mechanical Engineers to develop standardized methods for sampling and analysis of residual combustion products for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in municipal waste fired combustion emissions. The sampling protocols for this study were essentially identical to the proposed ASME/EPA/DOE protocol. The analytical protocols were also quite similar with the exception of the requirement of additional isotopically labelled internal standards which were not available in 1980.

Aldehyde Measurements--

Aldehydes in the stack emissions of the refuse-to-energy units were determined by an adaptation of the method described by Riggin (17). Two aldehyde determinations were performed at the RDF and modular units and three determinations were performed at the mass burning unit.

The emission sampling was performed with a midget impinger train of the type described in EPA Method 6 (10). A solution of 10 ml of 2 N HCl/0.05% 2,4-dinitrophenyl-hydrazine (DNPH) and 10 ml of isooctane was used in the first two impingers of the sampling train. Sampling times ranged from 30 to 60 minutes and total sample volumes collected ranged from 0.04 to 0.07 dscm.

The DNPH derivatives of the aldehydes and ketones were analyzed by reversed phase high performance liquid chromatography (HPLC) using an ultraviolet adsorption detector operated at 370 nm.

The two serial impinger samples from one test at the mass burning unit were analyzed separately to demonstrate that the aldehydes of interest were being quantitatively collected by the sampling train.

Organic Screening Analysis--

An analysis to screen for organic compounds in the refuse-to-energy unit emission samples was performed by HRGC/MS. The samples used for the analysis were aliquots of the PAH extracts of particulate material and XAD-2 traps taken before the silica gel cleanup step. The HRGC/MS analytical conditions used were the same as those employed for the PAH analysis. The organic compounds in the samples were tentatively identified using a forward search of the EPA/NIH library which contains spectra of approximately 32,000 compounds. Estimates of concentration levels of the various compounds in the samples were obtained by comparing the total ion current of the subject peak to that of the D_{12}-perylene internal standard and assuming a response factor of unity.

Volatile Organic Compounds--

Volatile hydrocarbons and chlorinated organic compounds were determined in the emissions of the mass burning unit. Samples of the gaseous emissions were extracted from the stack through a heated probe and a heated quartz fiber filter with a metal bellows pump. The samples were collected under approximately one atmosphere pressure in 4-liter stainless steel cannisters, the inside surfaces of which were electropolished to minimize sample-wall interactions.

The gas chromatographic system described by McClenny, et al (18), was used to identify and quantify volatile organic compounds in the gas samples. The analyses were performed by cryogenically concentrating a known volume of the gas sample, thermal desorption of the sample from the cryogenic trap, and separation of the organic compounds on a temperature-programmed, OV-1 fused silica capillary column. Flame ionization (FID) and electron capture (ECD) detectors were used to determine hydrocarbons and chlorinated organic compounds, respectively. Retention time data were used to identify compounds in the samples and quantitation was performed by comparing peak areas obtained with an electronic integrator to peak areas obtained with standard gas mixtures.

SECTION 5

RESULTS AND DISCUSSION

The results of the emission measurements performed on the refuse-to-energy incinerator systems are reported in the following sections. In the concluding section, a discussion and summary of the study results and similar data obtained by other investigators are presented.

PARTICULATE MASS AND SIZE DISTRIBUTION

The particulate mass concentrations measured in the emissions from the RDF, MASS, and MOD units using EPA Method 5 are shown in Tables 3, 4, and 5, respectively. Additional mass concentration data obtained from the SASS tests are presented in Tables 6, 7, and 8. Tables 3 through 8 also show the sampling train operating conditions and some of the operating parameters of the incinerator units.

Based on the Method 5 data, the mass concentration of particulate material in the RDF emissions ranged from 272 to 441 mg/dscm and the emission rate ranged from 22.4 to 36.1 kg/hr. For the MASS unit, the extremes in particulate mass concentration were approximately 261 and 599 mg/dscm and the extremes in particulate mass emission rate were 5.2 and 13.7 kg/hr. The particulate emissions of the MOD unit based on two valid tests ranged from approximately 153 to 261 mg/dscm in mass concentration and from 2 to 3.6 in mass emission rate.

Particulate size distribution data obtained for the three incinerator units are shown in Figures 2, 3, and 4. From the curves shown in the figures, it is evident that the emissions from none of the units follow a log-normal distribution. The approximate mass median diameter of the particulate emissions determined by measurements made with an Andersen impactor were: 6 μm for the RDF unit, 12 μm for the MASS unit, and 0.8 μm or less for the MOD unit. The RDF and MASS units were equipped with an electrostatic precipitator.

INORGANIC CHARACTER OF EMISSIONS

Elemental and Anion Composition of Particulate Material

The elemental content of particulate emission samples obtained from the RDF, MASS, and MOD refuse-to-energy units is shown in Tables 9, 10, and 11, respectively. Elements detected in the particulate emissions of the three

TABLE 3. SUMMARY OF METHOD 5 SAMPLING DATA--RDF UNIT

Test Parameter	Test 1	Test 2	Test 3
Test date	5-19-81	5-28-81	5-28-81
Sampling time, minutes	120	120	120
No. traverse points	20	20	20
Sample volume, dscm	2.443	2.414	2.286
Percent isokinetic sampling rate	104.7	101.0	97.4
Avg. temperatures, C - probe	123	140	148
- filter box	120	121	119
Avg. flue gas temperature, C	241	226	232
Flue static pressure, mm Hg[a]	-8.6	-8.6	-7.8
O_2, % by volume (dry)	11.7	15.0	11.3
CO_2, % by volume (dry)	6.8	9.5	8.0
Moisture, % by volume	12.7	9.7	11.3
Avg. flue gas velocity (V_s), m/s	18.15	17.61	17.72
Avg. volumetric flow (Q_{sd}), dscm/hr	81,845	85,243	82,411
Filter catch, mg	907.0	711.9	530.0
Probe/filter rinse catch, mg	170.4	79.5	90.9
Mass concentration, mg/dscm	441.0	327.8	271.6
Mass emission rate, Kg/hr	36.1	27.9	22.4

(a) Difference between stack and atmospheric pressure.

TABLE 4. SUMMARY OF METHOD 5 SAMPLING DATA--MASS BURNING UNIT

Test Parameter	Test 1	Test 2	Test 3
Test date	4-14-82	4-15-82	4-15-82
Sampling time, minutes	120	120	120
No. traverse points	8	8	8
Sample volume, dscm	2.570	2.636	2.650
Percent isokinetic sampling rate	108.9	99.1	97.5
Avg. temperatures, C - probe	139	148	152
- filter box	120	127	123
Avg. flue gas temperature, C	266	271	272
Flue static pressure, mm Hg(a)	-1	-1	-1
O_2, % by volume (dry)	7.0	7.7	8.5
CO_2, % by volume (dry)	13.3	11.3	11.7
Moisture, % by volume	17.4	15.1	14.8
Avg. flue gas velocity (V_s), m/s	10.50	11.61	11.81
Avg. volumetric flow (Q_{sd}), dscm/hr	19,864	22,409	22,880
Filter catch, mg	507.0	826.6	1,198.0
Probe/filter rinse catch, mg	170.5	215.7	390.3
Mass concentration, mg/dscm	261.2	395.4	599.4
Mass emission rate, Kg/hr	5.2	8.9	13.7

(a) Difference between stack and atmospheric pressure.

TABLE 5. SUMMARY OF METHOD 5 SAMPLING DATA--MODULAR UNIT

Test Parameter	Test 1	Test 2	Test 3
Test date	6-22-82	6-23-84	6-23-84
Sampling time, minutes	120	120	120
No. traverse points	8	8	8
Sample volume, dscm	1.700	1.588	1.604
Percent isokinetic sampling rate	110.7	109.1	110.3
Avg. temperatures, C - probe	126	126	125
- filter box	119	116	123
Avg. flue gas temperature, C	246	257	260
Flue static pressure, mm Hg[a]	-3.8	-3.8	-3.8
O_2, % by volume (dry)	12.9	12.4	13.0
CO_2, % by volume (dry)	7.0	7.1	7.0
Moisture, % by volume	15.3	14.7	14.4
Avg. flue gas velocity (V_s), m/s	9.66	9.50	9.29
Avg. volumetric flow (Q_{sd}), dscm/hr	14,047	13,668	13,326
Filter catch, mg	138.4[b]	344.6	193.4
Probe/filter rinse catch, mg	58.7[b]	69.1	52.3
Mass concentration, mg/dscm	115.9[b]	260.5	153.2
Mass emission rate, Kg/hr	1.6[b]	3.6	2.0

(a) Difference between stack and atmospheric pressure.

(b) Result may be low; indication of filter leakage during test.

TABLE 6. SUMMARY OF SASS SAMPLING DATA--RDF UNIT

Test Parameter	Test 1	Test 2	Test 3
Test date	5-19-81	5-21-81	5-26-81
Sampling time, minutes	165	180	180
Sample volume, dscm	14.90	17.06	16.51
Percent isokinetic sampling rate	127	134	129
Avg. temperatures, C - probe	228	222	215
- cyclones	198	202	204
- filter	207	204	204
- XAD-2 module	23	26	26
- impingers	19	19	22
Avg. flue gas temperature, C	259	253	251
Flue static pressure, mm Hg[a]	-8.6	-8.6	-8.6
O_2, % by volume	10.0	15.0	8.5
CO_2, % by volume	9.8	8.3	4.0
Moisture, % by volume	13.3	9.8	10.5
10 μm cyclone catch, mg	(b)	(b)	(b)
3 μm cyclone catch, mg	2,082.4	1,032.9	1,639.1
1 μm cyclone catch, mg	1,719.1	1,536.8	1,841.2
Filter catch, mg	5,030.9	2,707.3	1,680.8
Rinse residue, mg	252.3	165.1	283.4
Total particulate catch, mg	9,084.7	5,442.1	5,444.5
Mass concentration, mg/dscm[c]	609.7	319.0	329.8

(a) Difference between stack and atmospheric pressure.

(b) 10 μm cyclone was not used during these tests.

(c) Mass concentration may not be as representative of the source emissions as the Method 5 data since the SASS sampling was performed at a single point in the stack.

TABLE 7. SUMMARY OF SASS SAMPLING DATA--MASS BURNING UNIT

Test Parameter	Test 1	Test 2	Test 3
Test date	4-16-82	4-17-82	4-19-82
Sampling time, minutes	150	120	120
Sample volume, dscm	14.487	11.855	11.271
Percent isokinetic sampling rate	181	142	130
Avg. temperatures, C - probe	238	242	238
- cyclones	203	202	198
- filter	206	210	207
- XAD-2 module	17	19	14
- impingers	19	21	16
Avg. flue gas temperature, C	264	275	266
Flue static pressure, mm Hg(a)	-1	-1	-1
O_2, % by volume	7.7	7.7	7.7
CO_2, % by volume	12.1	12.1	12.1
Moisture, % by volume	15.3	16.3	14.6
10 μm cyclone catch, mg	3,510.8	2,606.1	4,056.5
3 μm cyclone catch, mg	979.7	881.7	640.4
1 μm cyclone catch, mg	1,967.4	1,417.3	1,953.0
Filter catch, mg	1,077.1	928.2	848.5
Rinse residue, mg	146.3	50.1	44.3
Total particulate catch, mg	7,681.3	5,883.4	7,542.7
Mass concentration, mg/dscm(b)	530.2	496.3	669.2

(a) Difference between stack and atmospheric pressure.

(b) Mass concentration may not be as representative of the source emissions as the Method 5 data since the SASS sampling was performed at a single point in the stack.

TABLE 8. SUMMARY OF SASS SAMPLING DATA--MODULAR UNIT

Test Parameter	Test 1	Test 2
Test date	6-25-82	6-27-82
Sampling time, minutes	160	134
Sample volume, dscm	15.083	12.897
Percent isokinetic sampling rate	346	172
Avg. temperatures, C - probe	203	204
- cyclones	203	202
- filter	202	207
- XAD-2 module	17	17
- impingers	26	24
Avg. flue gas temperature, C	196	224
Flue static pressure, mm Hg(a)	-3.8	-3.8
O_2, % by volume	12.8	12.8
CO_2, % by volume	7.0	7.0
Moisture, % by volume	10.9	13.2
10 μm cyclone catch, mg	(b)	(b)
3 μm cyclone catch, mg	650.4	3,482.1
1 μm cyclone catch, mg	576.6	760.1
Filter catch, mg	1,115.3	1,014.2
Rinse residue, mg	175.9	121.1
Total particulate catch, mg	2,518.2	5,377.5
Mass concentration, mg/dscm(c)	167.0	417.0

(a) Difference between stack and atmospheric pressure.

(b) 10 μm cyclone was not used during these tests.

(c) Mass concentration may not be as representative of the source emissions as the Method 5 data since the SASS sampling was performed at a single point in the stack.

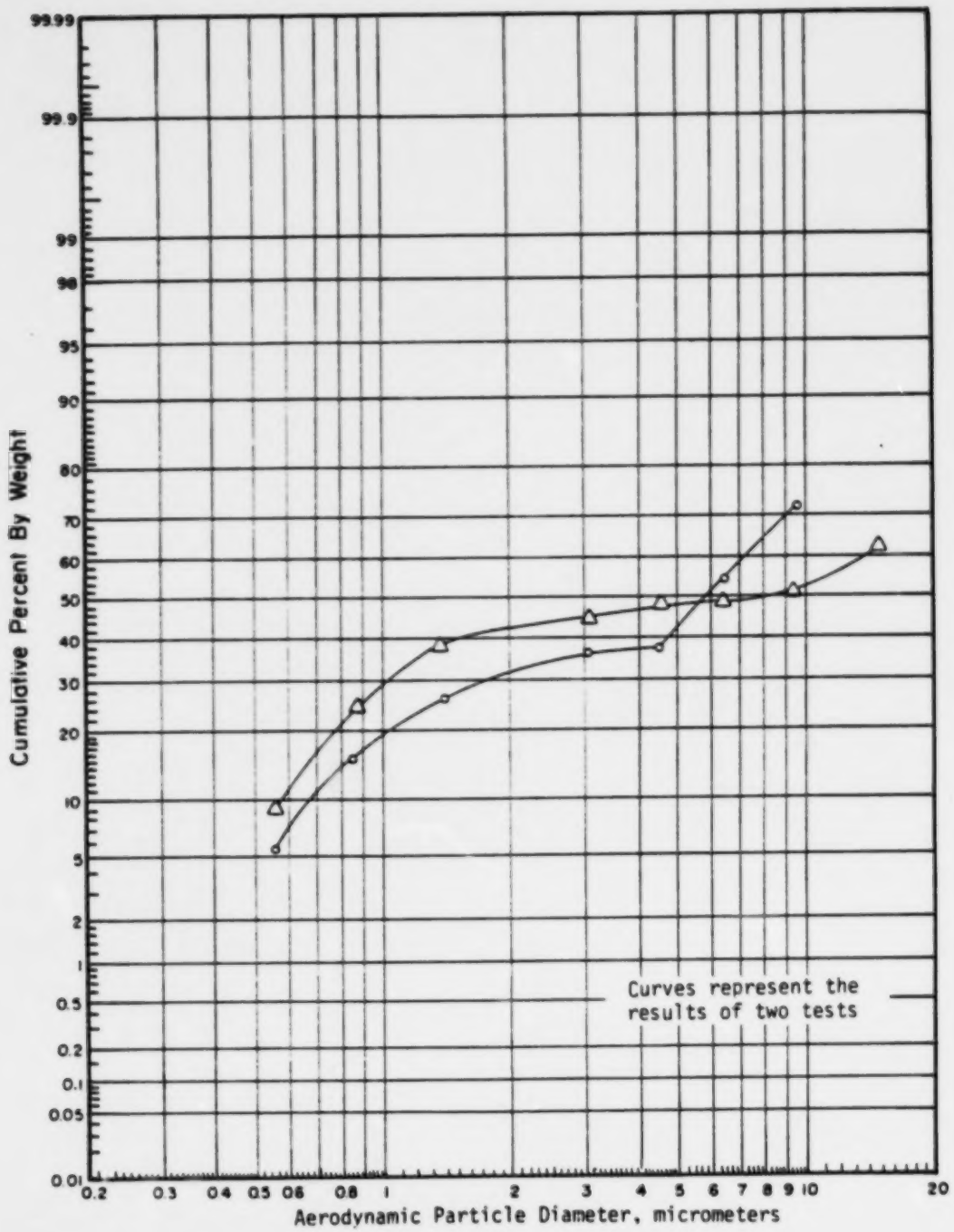

Figure 2. Aerodynamic size distribution of particulate emissions from refuse-derived fuel unit.

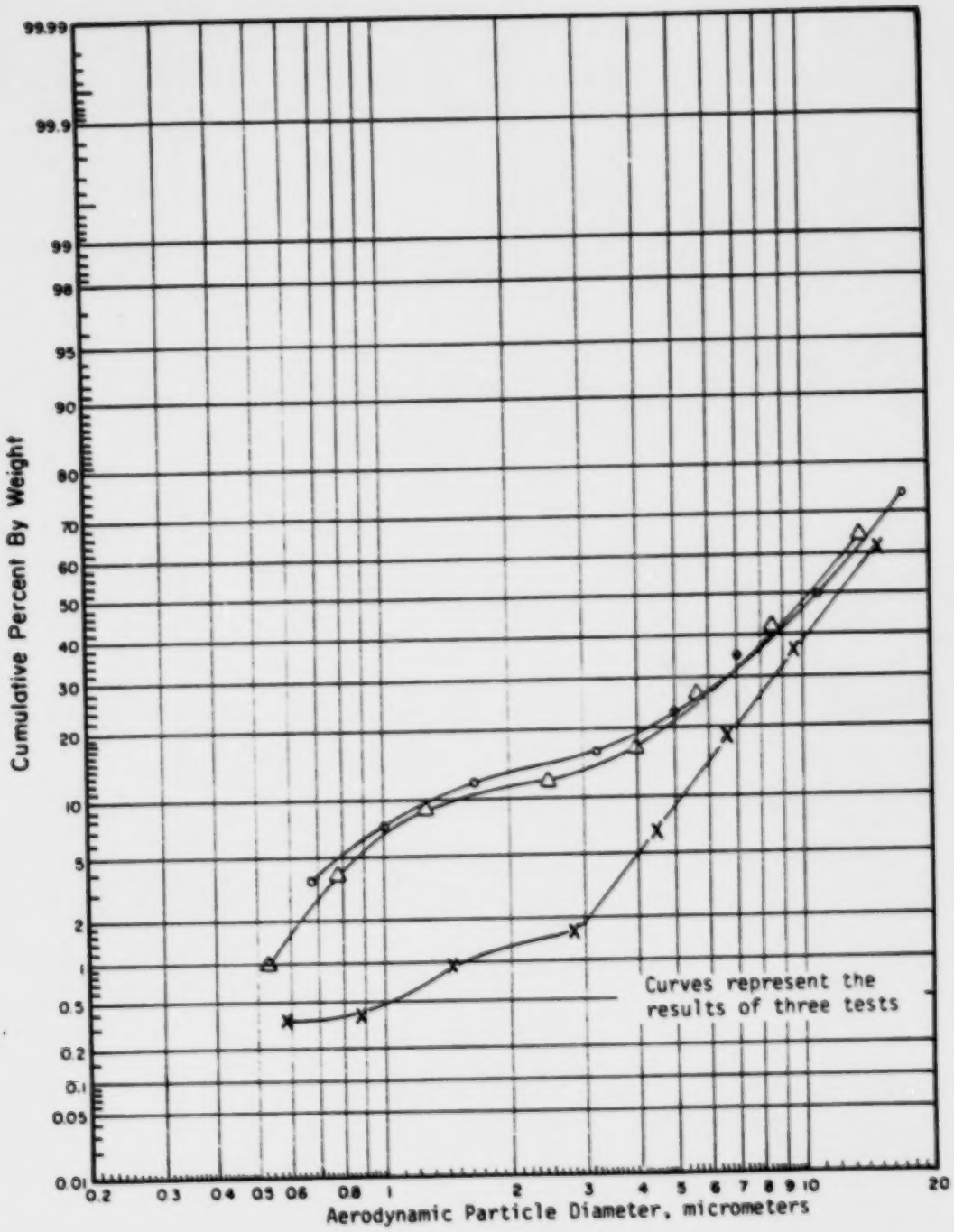

Figure 3. Aerodynamic size distribution of particulate emissions from mass burning unit.

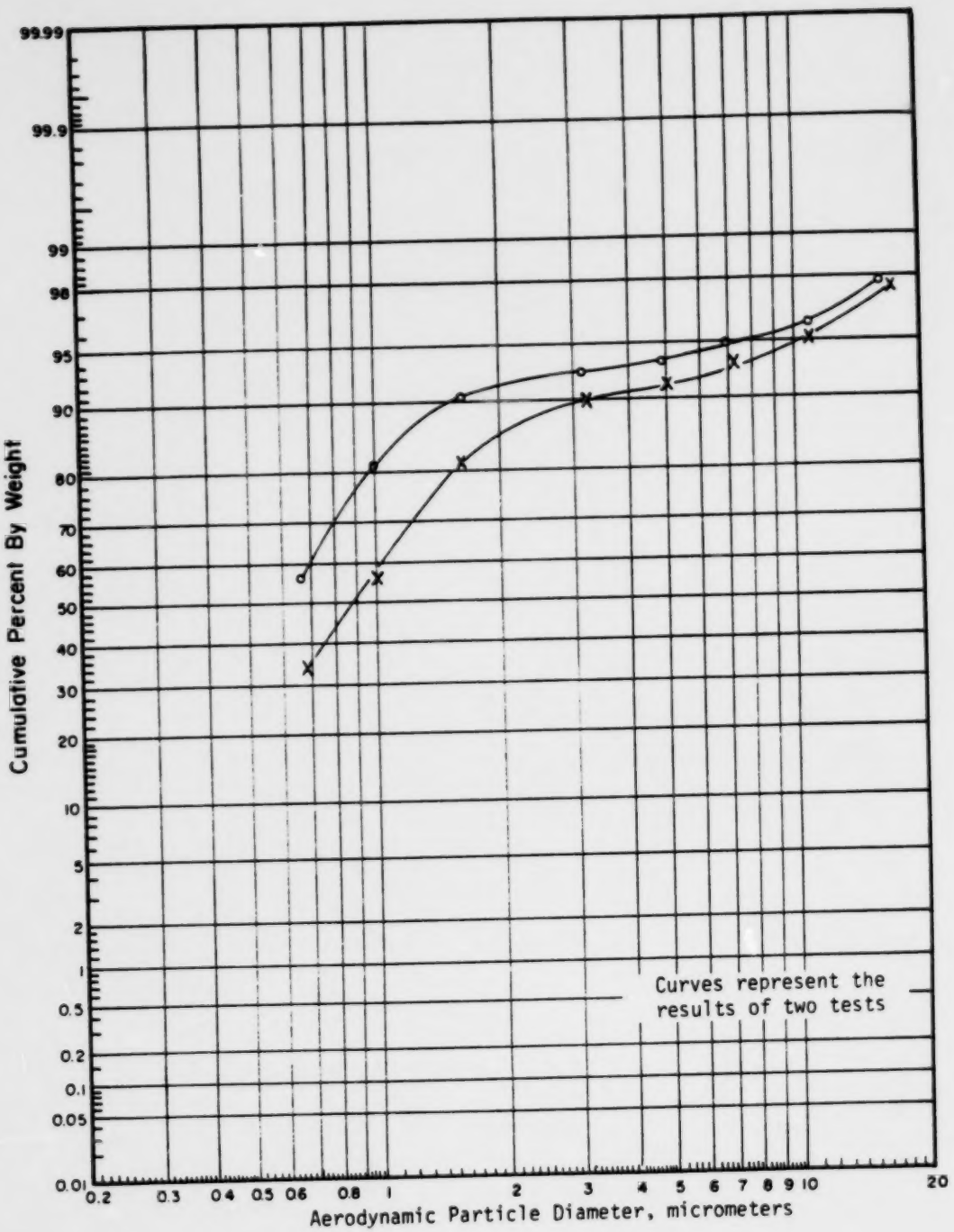

Figure 4. Aerodynamic size distribution of particulate emissions from modular unit.

TABLE 9. ELEMENTAL COMPOSITION OF PARTICULATE STACK EMISSIONS FROM RDF UNIT[a]

Element[b]	Test No. 1		Test No. 2		Test No. 3	
	µg/g	µg/dscm	µg/g	µg/dscm	µg/g	µg/dscm
H+	3500	2100	4300	1400	<1000	<330
Li	9	6	18	6	18	6
Be	(b)	(b)	(b)	(b)	(b)	(b)
B	120	70	120	40	18	6
C+	320000	200000	291000	93000	70000	2300
N+	<1000	<600	<1000	<300	<1000	<330
F	400	240	80	30	120	40
Na*	64000	39000	55000	18000	24000	79000
Mg*	5900	3600	6300	2000	2900	960
Al*	27000	16000	28000	8900	9100	3000
Si*	49800	30000	53000	17000	18000	5900
P*	1800	1100	1800	570	2000	660
S*	45000	27000	54000	17000	91000	30000
Cl*	68000	41000	45000	14000	250000	82000
K*	61000	37000	71000	23000	107000	35000
Ca*	28000	17000	299000	9300	11000	3600
Sc	3	2	4	1	1	0.4
Ti*	8100	4900	7100	2300	2600	860
V	60	40	60	20	2	0.7
Cr*	700	430	980	310	500	160
Mn*	960	590	11000	3500	600	200
Fe*	10400	6300	11000	3500	5600	1800
Co	40	24	40	13	10	3
Ni*	200	120	300	100	100	30
Cu*	800	490	1100	350	1500	490
Zn*	12500	7600	15000	4800	15000	4900
Ga	12	7	8	3	4	1
Ge	6	4	2	0.6	2	0.7
As	400	240	60	20	20	7
Se	<8	<5	<24	<8	<24	<8
Br*	1800	1100	1400	450	5500	1800
Rb	200	120	70	20	20	7
Sr	50	30	30	10	3	1
Y	1	0.6	1	0.3	0.2	0.1
Zr	60	40	18	6	2	0.6
Nb	6	4	1	0.4	1	0.3
Mo	40	24	20	6	4	1

TABLE 9. (Continued)

Element(b)	Test No. 1		Test No. 2		Test No. 3	
	µg/g	µg/dscm	µg/g	µg/dscm	µg/g	µg/dscm
Ru	<6	<4	<0.6	<0.2	<0.6	<0.2
Rh	<6	<4	<6	<2	<6	<2
Pd	<0.4	<0.2	<0.4	<0.1	<0.4	<0.1
Ag	60	37	14	4	6	2
Cd*	400	240	500	160	1000	330
In	<4	<2	<4	<1	<4	<1
Sn*	1300	790	1700	540	1900	630
Sb*	500	300	600	190	700	230
Te	<0.4	<0.2	<0.4	<0.1	<0.4	<0.1
I	60	35	3	1	<0.9	<0.3
Cs	7	4	2	0.6	0.7	0.2
Ba	700	430	500	160	600	200
La	4	2	0.4	0.1	0.6	0.2
Ce	4	2	1	0.4	0.4	0.1
Pr	2	1	0.4	0.1	<0.2	<0.1
Nd	<1	<0.6	<1	<0.3	<1	<0.3
Sm	<0.6	<0.4	<0.6	<0.2	<0.6	<0.2
Eu	<0.4	<0.2	<0.4	<0.1	<0.4	<0.1
Gd	<0.6	<0.4	<0.6	<0.2	<0.6	<0.2
Tb	<1	<0.6	<0.1	<0.04	<0.1	<0.04
Dy	<0.6	<0.4	<0.6	<0.2	<0.6	<0.2
Ho	<0.2	<0.1	<0.2	<0.1	<0.2	<0.01
Er	<0.4	<0.2	<0.4	<0.1	<0.4	<0.1
Tm	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Yb	<0.6	<0.4	<0.6	<0.2	<0.6	<0.2
Lu	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Hf	<3	<2	<0.3	0.1	<3	<1
Ta	<60	<40	<12	<4	<2	<0.7
W	4	2	<1	<0.3	<1	<0.3
Re	<0.6	<0.4	<0.6	<0.2	<0.6	<0.2
Os	<0.6	<0.4	<0.6	<0.2	<0.6	<0.2
Ir	<0.4	<0.2	<0.4	<0.1	<0.4	<0.1
Pt	<0.6	<0.4	<0.6	<0.2	<0.6	<0.2
Au	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Tl	0.4	0.2	0.4	0.1	0.4	0.1
Pb*	11000	6700	13000	4100	24000	7900
Bi	2	1	0.6	0.2	0.6	0.2
Th	0.6	0.4	0.6	0.2	0.6	0.2
U	1	0.7	0.6	0.2	0.6	0.2

(a) Reported as µg of element/gram of fly ash and µg of element/dry, standard cubic meter of stack gas

(b) + Elements determined by combustion with Perkin Elmer 240 Analyzer
* Elements determined by XRF
All other elements determined by spark source mass spectrometry.

TABLE 10. ELEMENTAL COMPOSITION OF PARTICULATE STACK EMISSIONS FROM MASS BURNING UNIT(a)

Element(b)	Test No. 1		Test No. 2		Test No. 3	
	µg/g	µg/dscm	µg/g	µg/dscm	µg/g	µg/dscm
H+	4000	2100	3000	1490	3000	2000
Li	10	5	10	5	20	13
Be	0.05	0.03	0.03	0.01	0.03	0.02
B	30	16	30	15	60	40
C+	254000	135000	191000	94700	235000	157000
N+	<1000	<530	<1000	<500	<1000	<670
F	80	40	200	100	80	50
Na*	46800	24800	40500	20100	46100	30900
Mg*	4900	2600	6200	3080	5600	3570
Al*	23700	12600	27700	13700	26500	17700
Si*	53100	28100	64200	31800	65600	43900
P*	4900	2600	6200	3080	5900	3950
S*	22600	12000	27200	13500	20300	13600
Cl*	136000	72100	110800	55000	125000	83700
K*	60000	31800	69600	34500	55200	36900
Ca*	36200	19200	50400	25000	42400	28400
Sc	<3	<2	<3	<1	<3	<2
Ti*	9200	48800	9900	4910	8200	5490
V	40	20	100	50	40	27
Cr*	500	270	450	220	560	370
Mn*	900	480	980	490	850	570
Fe*	7900	4190	8400	4170	9000	6020
Co	20	11	40	20	40	27
Ni*	400	210	400	200	400	270
Cu*	780	410	770	380	950	640
Zn*	44000	23300	26600	13200	30000	20100
Ga	30	16	30	15	15	10
Ge	10	5	10	5	10	7
As*	300	160	130	64	710	480
Se	<30	<16	<30	<15	<30	<20
Br*	1700	900	1300	640	1500	1000
Rb	100	53	70	35	100	67
Sr	70	37	50	25	50	33
Y	4	2	2	1	2	1
Zr	60	32	30	15	20	13
Nb	6	3	4	2	2	1
Mo	20	11	20	10	15	10

TABLE 10. (Continued)

Element(b)	Test No. 1		Test No. 2		Test No. 3	
	µg/g	µg/dscm	µg/g	µg/dscm	µg/g	µg/dscm
Ru	<0.6	<0.3	<0.6	<0.3	<0.6	<0.4
Rh	<6	<3	<6	<3	<6	<4
Pd	<2	<1	<2	<1	<2	<1
Ag	150	80	100	50	40	27
Cd*	970	510	780	390	910	610
In	40	21	40	20	20	13
Sn*	5000	2650	4300	2130	3600	2410
Sb*	880	470	740	370	990	660
Te	<0.6	<0.3	<0.6	<0.3	<0.6	<0.4
I	20	11	15	7	6	4
Cs	5	2	5	2	2	1
Ba*	2900	1540	980	490	1300	870
La	4	3	4	2	2	1
Ce	10	5	10	5	2	1
Pr	2	1	2	1	1	0.5
Nd	20	11	10	5	10	7
Sm	<1	<0.5	<1	<0.5	<1	<0.7
Eu	<0.4	<0.2	<0.4	<0.2	<0.4	<0.3
Gd	<0.6	<0.3	<0.6	<0.3	<0.6	<0.4
Tb	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Dy	<0.6	<0.3	<0.6	<0.3	<0.6	<0.4
Ho	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Er	<0.4	<0.2	<0.4	<0.2	<0.4	<0.3
Tm	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Yb	<1.5	<0.8	<1.5	<0.7	<1.5	<1
Lu	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Hf	<3	<2	<3	<1	<3	<2
Ta	<0.4	<0.2	<0.4	<0.2	<0.4	<0.3
W	<0.6	<0.3	<0.6	<0.3	<0.6	<0.4
Re	<0.4	<0.2	<0.4	<0.2	<0.4	<0.3
Os	<0.6	<0.3	<0.6	<0.3	<0.6	<0.4
Ir	<0.4	<0.2	<0.4	<0.2	<0.4	<0.3
Pt	<0.6	<0.3	<0.6	<0.3	<0.6	<0.4
Au	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Tl	1	0.5	3	<1	1	0.5
Pb*	20700	11000	14400	7140	16000	10700
Bi	150	80	40	20	60	40
Th	<0.4	<0.2	<0.4	<0.2	<0.4	<0.3
U	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1

(a) Reported as µg of element/gram of fly ash and µg of element/dry, standard cubic meter of stack gas

(b) + Elements determined by combustion with Perkin Elmer 240 Analyzer
* Elements determined by XRF
All other elements determined by spark source mass spectrometry.

TABLE 11. ELEMENTAL COMPOSITION OF PARTICULATE STACK EMISSIONS FROM MODULAR UNIT[a]

Element	Test No. 1[b]		Test No. 2[c]	
	µg/g	µg/dscm	µg/g	µg/dscm
H+	NA	NA	2000	910
Li	30	5	100	46
Be	0.2	0.03	0.3	0.1
B	150	25	150	68
C+	NA	NA	31000	14100
N+	NA	NA	<1000	<455
F	60	10	200	91
Na*	60000	10000	21900	10000
Mg*	10000	1700	17100	7790
Al*	50000	8300	65900	30000
Si*	70000	12000	115000	52400
P*	2500	420	2700	1230
S*	10000	1700	27600	12600
Cl*	10000	1700	27800	12700
K*	70000	12000	20100	9150
Ca*	30000	5000	50500	23000
Sc	<0.5	<0.1	<2	<1
Ti*	6000	1000	12700	5780
V	30	5	30	14
Cr*	1000	170	640	290
Mn*	300	50	940	430
Fe*	25000	4200	12300	5600
Co	10	2	10	5
Ni	500	83	100	46
Cu*	300	50	500	230
Zn*	30000	5000	53600	24400
Ga	6	1	3	1
Ge	<3	<0.5	<0.2	<0.1
As*	30	5	280	130
Se	<15	<3	<15	<7
Br*	4000	670	9300	4200
Rb	50	8	30	14
Sr	30	5	30	14
Y	3	0.5	2	1
Zr	100	17	100	46
Nb	3	0.5	5	2
Mo	20	3	10	5

TABLE 11. (Continued)

Element	Test No. 1(b) µg/g	Test No. 1(b) µg/dscm	Test No. 2(c) µg/g	Test No. 2(c) µg/dscm
Ru	<0.2	<0.03	<0.2	<0.1
Rh	<0.5	<0.08	<0.5	<0.2
Pd	<0.3	<0.05	<0.3	<0.1
Ag	30	5	10	5
Cd*	100	17	570	260
In	10	2	10	5
Sn*	1000	170	2200	1000
Sb*	1000	170	15300	7000
Te	<0.2	<0.03	<0.2	<0.1
I	<0.1	<0.02	<0.1	<0.05
Cs	4	0.7	4	2
Ba*	700	120	1200	550
La	7	1	7	3
Ce	10	2	10	5
Pr	1	0.2	1	0.5
Nd	<0.5	<0.08	<0.5	<0.2
Sm	<0.5	<0.08	<0.5	<0.2
Eu	<0.2	<0.03	<0.2	<0.1
Gd	<0.3	<0.05	<0.3	<0.1
Tb	<0.1	<0.02	<0.1	<0.05
Dy	<0.3	<0.05	<0.3	<0.1
Ho	<0.1	<0.02	<0.1	<0.05
Er	<0.2	<0.03	<0.2	<0.1
Tm	<0.1	<0.02	<0.1	<0.05
Yb	<0.3	<0.05	<0.3	<0.1
Lu	<0.1	<0.02	<0.1	<0.05
Hf	<2	<0.3	<2	<1
Ta	<0.6	<0.1	<0.4	<0.2
W	5	0.8	0.5	0.2
Re	<0.2	<0.03	<0.2	<0.1
Os	<0.3	<0.05	<0.3	<0.1
Ir	<0.3	<0.05	<0.3	<0.1
Pt	<0.3	<0.05	<0.3	<0.1
Au	<0.1	<0.02	<0.1	<0.05
Tl	0.4	0.07	0.4	0.2
Pb*	10000	1670	35000	16000
Bi	3	0.5	3	1
Th	<0.3	<0.05	<0.3	<0.1
U	<0.3	<0.05	<0.3	<0.1

(a) Reported as µg of element per gram of fly ash and µg of element (in particulates) per dry, standard cubic meter of stack gas.

(b) All elements determined by spark source mass spectrometry in Test 1 sample.

c) + elements determined by combustion with Perkin-Elmer 240 analyzer (Test 2 only).
* elements determined by XRF (Test 2 only).
All other elements in Test 2 sample determined by spark source mass spectroscopy.

units at levels of 10 percent by weight or higher were C and Cl. Those generally present at or above 1 percent by weight were Ca, Zn, Fe, S, Si, K, Al, Na, and Pb.

The anionic composition of fly ash samples from the three units are shown in Table 12. The principal anions common to samples from all three units were sulfate, chloride, and bromide. Fly ash solubility data are also shown in Table 12. The soluble fraction of the fly ash from the three units varied from approximately 13 to 77 percent by weight with the MOD sample exhibiting the least solubility. The total sulfur data given in the table was obtained by combustion. These values show good agreement with the XRF results given in Tables 9 through 11.

Volatile Trace Elements

Table 13 shows the concentrations of volatile trace elements measured in the stack emission of the three incinerator units. The most abundant element was Hg which was found at widely varying levels; 16 to 6250 µg/dscm. Concentrations of As, Se, Sb, and Pb were generally less than 10 µg/dscm, although Sb was detected at a concentration of 42 µg/dscm in one of the MASS samples.

Gaseous HCl and HF Emissions

Data on the concentration of gaseous HCl and HF found in the incinerator emissions are presented in Table 14. Levels of HCl ranging from 352 to 516 mg/dscm (263 to 340 ppm) were measured in the RDF and MASS units. Lower levels of HCl, 53 to 231 mg/dscm (35 to 153 ppm), were detected in the MOD emissions. The concentration of HF in the emissions of the three units was fairly uniform, ranging from 0.3 to 1.4 mg/dscm (0.4 to 1.7 ppm).

Compound Identification

The results of the infrared analysis of emission samples from the refuse-to-energy units are summarized in Table 15. The infrared spectra of the various samples are presented in Appendix A. Identification of compounds in the particulate emission samples from the three units are given as positive, probable or possible. In all cases, those identifications which are only tentative (marked possible) are of minor or trace components; because the component is present in such low concentration, a positive identification is not possible.

The three samples are similar in composition in that they are mixtures of sulfates, silicates and quartz. Perhaps more striking is the number of possible compound types not present, in particular, metal oxides. Most fly ashes from combustion sources contain significant quantities of metal oxides, primarily ferrous, ferric and aluminum oxides. These samples contain neither these nor any other oxide with the possible exception of the oxides which adsorb only in the far infrared region. In addition, though less surprising, these samples show no indication of nitrates, phosphates or ammonium compounds which are also frequently found in fly ash.

TABLE 12. ANION COMPOSITION OF FLY ASH FROM REFUSE-TO-ENERGY UNITS

Unit	Test No.	Fly Ash Composition, Percentage by Weight							
		$SO_4^=$	Total S[a]	NO_3^-	Cl^-	F^-	Br^-	$PO_4^=$	Insolubles
RDF	1	10.39	4.0	<0.01	7.98	0.10	0.23	0.001	66.8
	2	14.57	5.0	<0.01	5.80	0.06	0.13	0.010	70.5
	3	25.12	7.6	<0.01	25.4	0.06	0.75	0.003	22.6
MASS	1	5.82	1.6	<0.01	13.03	0.07	0.17	0.007	63.2
	2	8.09	2.1	<0.01	12.26	0.04	0.14	0.005	60.6
	3	6.27	1.6	<0.01	14.69	0.06	0.20	0.002	59.3
MOD	2	7.22	2.6	<0.01	3.40	0.04	1.09	0.001	87.3

(a) Determined by combustion.

TABLE 13. VOLATILE TRACE ELEMENTS IN STACK EFFLUENTS

Unit	Test No.	Concentration in Stack Gas, µg/dscm				
		As	Se	Hg	Sb	Pb
RDF	1	0.3	0.3	30	0.9	2.3
	2	3.8	0.4	169	1.1	1.1
	3	<0.2	1.4	193	3.7	0.9
MASS	1	<0.2	0.7	6250	7.3	<0.7
	2	<0.2	0.9	656	5.1	3.7
	3	2.3	<0.5	291	42	<0.5
MOD	1	<0.3	<0.5	136	<2	6.3
	2	<0.3	<0.5	16	<2	4.6

TABLE 14. HCl AND HF EMISSION DATA

Unit	Test No.	Concentration in Stack Gas, mg/dscm(ppm) HCl	HF
RDF	1	516(340)	1.2(1.4)
	2	352(232)	1.2(1.4)
MASS	1	400(263)	1.4(1.7)
	2	427(282)	0.8(1.0)
MOD	1	53(35)	0.3(0.4)
	2	231(153)	0.8(0.9)

TABLE 15. INFRARED ANALYSIS RESULTS

Sample	Major Components		Minor Components	
	Identification	Confidence	Identification	Confidence
RDF	K_2SO_4	positive	quartz	positive
	Na_2SO_4	positive	$XHCO_3$ (trace)	probable
	Metal silicates (probably as Al)	positive	$AlK(SO_4)_2$	probable
			$CaSO_4$ (trace)	possible
			X_2SO_4	probable
MASS	quartz	positive	$XHCO_3$	probable
	$CaSO_4$	positive	K_2SO_4	positive
	Metal silicates (probably as Al)	positive	X_1SO_4 (trace)	possible
MOD	Metal silicates (probably as Al)	positive	quartz	positive
			$XHCO_3$ (trace)	probable
	$CaSO_4$	positive	$AlK(SO_4)_2$ or $MgSO_4$	possible

As-Received Samples--

Spectra of the as-received fly ashes from the three units (Figures A-1 through A-3, Appendix A) indicate that these samples are primarily a mixture of sulfates and silicates as far as components which adsorb in the mid infrared are concerned. Reference to the elemental data indicates that these samples have other major constituents which may not contribute to the infrared spectra of the samples. For instance, RDF and MASS have 29.1 and 23.5 percent carbon respectively, largely as soot which does not have a mid infrared spectrum. In addition, all three samples contained significant concentrations of chlorides, many of which have no mid infrared spectrum.

The RDF sample showed a significantly higher sulfate to silicate ratio compared to the other two samples. This is confirmed by the elemental data. The MOD and RDF samples contain low amounts and the MASS sample a much greater concentration of crystalline quartz indicated by the doublet near 800 cm^{-1}.

The MASS sample has a band at 1400 cm^{-1} which could be a carbonate; neither RDF nor MOD have measurable bands in the carbonate region. None of the three samples show any evidence for nitrates or phosphates which is again supported by the elemental data. Finally, there is no evidence for any sizable concentration of organic material (that is, more than 2 or 3 percent maximum) in any of these samples.

Water Insolubles--

Spectra of the water insoluble portion (Figures A-4 through A-9) of all three samples indicate them to be primarily composed of metal silicates and quartz. From the elemental data, it is suspected that there would be quite a bit of aluminum incorporated as silicate; in fact, the amount of aluminum in the sample appears to be inversely proportional to the amount of quartz. That is, the proportion of Si-O which is due to metal silicate rather than quartz increases concurrently with aluminum concentration indicating that the aluminum is probably complexed with the silicate. It is most unusual that there is no indication of any free Al_2O_3 or any other oxide in any of the samples. As previously mentioned, all three samples contain some crystalline ( ) quartz as seen by the doublet near 800 cm^{-1}, although the concentration is quite low for RDF and MOD samples. All three samples contain a component with a band at 1440 cm^{-1}, with the MASS sample having by far the greater quantity of this component. This band, together with the band near 1600 cm^{-1}, has been seen previously in water insoluble samples and tentatively identified as an unknown bicarbonate, $XHCO_3$, although presence of a carbonate is also possible.

Water Solubles--

Spectra of the water-soluble fractions (Figures A-10 through A-15) indicate that samples from all three units contain primarily sulfates. Again, there is no spectral evidence for other commonly seen water soluble components: nitrate, carbonates, phosphates or organic compounds. In order to clearly resolve the overlapping sulfate bending bands in the 600 cm^{-1} region, deconvoluted spectra of both baked and unbaked water soluble samples were obtained (A-16, A-17, and A-18).

The predominate sulfate in the MASS water-soluble sample is $CaSO_4$. This can be seen by the bending vibrations at 600 and 670 cm^{-1} for $CaSO_4 \cdot 2H_2O$ as well as the very characteristic bands due to water of hydration at 3400 and 3550 cm^{-1}. On baking, some change to $CaSO_4 \cdot 1/2\ H_2O$ is seen both in the

disappearance of the bands due to waters of hydration and bands in the 600 cm^{-1} region which also indicate any additional change from $CaSO_4 \cdot 1/2\ H_2O$ in the unbaked sample to anhydrous $CaSO_4$. $CaSO_4$ is present both as the two hydrate and the half hydrate in unbaked sample; a shift can then be monitored on baking to a mixture of $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 1/2\ H_2O$, and anhydrous $CaSO_4$. K_2SO_4 is also present as seen by the band at 615 cm^{-1} but in much lower concentrations than $CaSO_4$.

There is probably one other sulfate present in trace concentration in the MASS sample. Band positions in the spectrum of the unbaked samples could indicate $ZnSO_4$. However, the component is not present at sufficient levels to permit definitive identification.

There are two major sulfates present in the RDF water-soluble sample. K_2SO_4 accounting for 1/2 to 2/3 of the sulfate present and Na_2SO_4 accounting for 1/3 to 1/2 of the sulfate present. K_2SO_4 has a single bending vibration at about 617 cm^{-1}; Na_2SO_4 has bending vibrations at about 615 and 640 cm^{-1} in both baked and unbaked samples. Deconvolution spectra shown in Figure A-17 exhibit band positions more clearly. Bands in the 600 cm^{-1} region in conjunction with the sulfate stretching vibration at 1185 cm^{-1} are indicative of the presence of $AlK(SO_4)_2$. $CaSO_4$ may be present in trace amounts and the intensity of the 660 cm^{-1} indicates the presence of an unknown sulfate (X_2SO_4). The unknown sulfate in the RDF sample is not the same as the unidentified sulfate in the MASS (X_1SO_4) sample.

MOD Water Solubles--

The MOD water soluble sample, like the MASS sample, has $CaSO_4$ as the major sulfate present. Deconvolution, seen in Figure A-18, shows that there are one or more additional sulfates present in low concentration. These bands, together with bands near 1100 cm^{-1} indicate the possible presence of $AlK(SO_4)_2$ and/or $MgSO_4$.

ORGANIC CHARACTER OF EMISSIONS

Polynuclear Aromatic Hydrocarbons (PAH)

Concentrations of PAH compounds found in the stack emissions of the refuse-to-energy systems are reported in Tables 16, 17, and 18. The levels vary widely for the same unit as well as among the three units. The lowest values were observed in the MOD emissions and the highest in the MASS emissions. Compounds present in emissions of all three units included: naphthalene, phenanthrene/anthracene, pyrene, acenapthylene. The higher molecular weight PAH compounds, e.g., benzopyrenes were detected only in the MASS emissions. Data for the RDF and MASS units shows that the PAH distribution in the emissions heavily favors the gas phase at the temperature maintained during sample collection (205°C). Separate analysis of the particulate and gas phase samples was not performed on the MOD samples.

TABLE 16. PAH CONCENTRATIONS IN STACK EMISSIONS FROM RDF UNIT

Compound	Concentration in Stack Emissions, ng/dscm[a]								
	Test No. 1			Test No. 2			Test No. 3		
	Part.	Gas	Total	Part.	Gas	Total	Part.	Gas	Total
Naphthalene	7	ND	7	12	6450	6462	ND	6300	6300
Methyl Naphthalenes	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dimethylnaphthalenes	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	40	ND	40	ND	4510	4510	ND	360	360
Acenaphthylene	ND	ND	ND	ND	530	530	ND	6	6
Fluorene	ND	ND	ND	ND	ND	ND	ND	6	6
Phenanthrene/Anthracene	47	200	247	88	3050	3138	24	12	36
Methyl Phenanthrene/Anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluoranthene	13	40	53	41	470	511	6	18	24
Pyrene	7	13	20	18	235	253	ND	6	6
Benzo(a)anthracene/chrysene	ND	7	7	ND	80	80	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(e)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(b or k)fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indenol(1,2,3,-cd)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND

(a) All data are corrected for blank levels.

ND - Not Detected; estimated minimum detectable concentration is 6 ng/dscm.

TABLE 17. PAH CONCENTRATIONS IN STACK EMISSIONS FROM MASS BURNING UNIT

Compound	Concentration in Stack Emissions, ng/dscm[a]								
	Test No. 1			Test No. 2			Test No. 3		
	Part.	Gas	Total	Part.	Gas	Total	Part.	Gas	Total
Naphthalene	9000	390000	399000	-	-	5600000	-	-	2100000
Methyl Naphthalenes	ND	ND	ND	-	-	160000	-	-	8900
Dimethylnaphthalenes	ND	ND	ND	-	-	ND	-	-	ND
Acenaphthene	ND	ND	ND	-	-	ND	-	-	ND
Acenaphthylene	ND	ND	ND	-	-	520000	-	-	1900000
Fluorene	ND	ND	ND	-	-	ND	-	-	ND
Phenanthrene/Anthracene	12000	150000	162000	-	-	2400000	-	-	410000
Methyl Phenanthrene/Anthracene	ND	ND	ND	-	-	ND	-	-	ND
Fluoranthene	ND	83000	83000	-	-	1500000	-	-	210000
Pyrene	ND	90000	90000	-	-	1600000	-	-	200000
Benzo(a)anthracene/chrysene	ND	4500	4500	-	-	52000	-	-	5900
Benzo(a)pyrene	ND	6800	6800	-	-	18000	-	-	2300
Benzo(e)pyrene	ND	7700	7700	-	-	45000	-	-	4700
Perylene	ND	1600	1600	-	-	22000	-	-	2800
Benzo(b or k)fluoranthene	ND	ND	ND	-	-	ND	-	-	ND
Indenol(1,2,3,-cd)pyrene	ND	ND	ND	-	-	ND	-	-	ND
Benzo(g,h,i)perylene	ND	ND	ND	-	-	ND	-	-	ND

(a) All data are corrected for blank levels.

ND - Not Detected; estimated minimum detectable concentration is 10 ng/dscm.

TABLE 18. PAH CONCENTRATIONS IN STACK EMISSIONS FROM MODULAR UNIT

Compound	Concentration in Stack Emissions, ng/dscm[a]	
	Test No. 1, Total	Test No. 2, Total
Naphthalene	3900	11000
Methyl Naphthalenes	2700	2600
Dimethylnaphthalenes	3600	1200
Acenaphthene	270	390
Acenaphthylene	270	540
Fluorene	200	230
Phenanthrene/Anthracene	1400	1300
Methyl phenanthrene/anthracene	ND	ND
Fluoranthene	130	390
Pyrene	70	230
Benzo(a)anthracene/chrysene	ND	ND
Benzo(a)pyrene	ND	ND
Benzo(e)pyrene	ND	ND
Perylene	ND	ND
Benzo(b or k)fluoranthene	ND	ND
Indenol(1,2,3,-cd)pyrene	ND	ND
Benzo(g,h,i)perylene	ND	ND

(a) All data are corrected for blank levels

ND - Not Detected; estimated minimum detectable concentration 10 ng/dscm.

Dioxins and Furans

Tables 19, 20, and 21 show the levels of tetrachlorodibenzo-p-dioxins (TCDD) and tetrachlorodibenzofurans (TCDF) in the stacks emissions of the three units. Data are reported for the 2,3,7,8-TCDD isomer and for total TCDD (sum of all isomers present). The 2,3,7,8-TCDF concentrations found in the MASS emissions are given and the total TCDF concentrations (sum of all isomers present) are reported. The number of TCDD and TCDF isomers detected in the samples is also shown.

The TCDD and TCDF data show considerable variation in levels among tests on the same unit and between units, however, the variations are not as great as observed for the PAH compounds. The average total TCDD concentrations measured in the RDF, MASS, and MOD stack emissions were 174, 245, and 11 ng/dscm, respectively. The 2,3,7,8-TCDD isomer constituted a significantly larger fraction of the total TCDD emission from MASS unit than from the other two incinerators. The average total TCDF emissions from the RDF, MASS, and MOD units were 458, 385, and 73 ng/dscm, respectively. The distribution of TCDD generally appears to favor the particulate phase although RDF Test No. 2 shows the major fraction in the gas phase. The TCDF data does not show a clear trend in distribution between the particulate and gaseous phases of the emissions.

Aldehydes

The concentrations of aldehydes found in the incinerator emissions are shown in Table 22. The data are characterized by large variations in aldehyde levels both within and between sites. Generally higher concentrations were observed in the MASS emissions. The MASS Test No. 2 data show that the aldehydes were efficiently collected by the impinger train.

Other Organic Compounds

The results of HRGC/MS organic screening analysis of the incineration stack emission samples are provided in Tables 23, 24, 25, and 26. Table 23 shows the tentative identification and estimated concentration of organic compounds detected in the RDF particulate emissions. Table 24 shows similar data for the RDF gas phase sample. Table 25 shows data obtained from combined particulate and gas phase samples from the MASS unit and Table 26 gives data on compounds found in the MOD particulate sample only. It is important to note that the data given in Tables 23 through 26 provide only a tentative identification of compounds present and a semi-quantitative estimate of the concentration in the emissions. Confirmation of compound identities was not performed and specific standards were not used to obtain the concentration data.

Volatile hydrocarbons detected in samples of the MASS emissions are shown in Table 27. Similar data were not obtained at the other two sites. The identity of the compounds listed in the table was determined by GC retention time and, therefore, should be considered tentative.

TABLE 19. TCDD AND TCDF EMISSIONS FROM RDF UNIT

Test No.	Sample Type	TCDD Concentration, ng/dscm		TCDF Concentration, ng/dscm	
		2,3,7,8-TCDD	Total TCDD[a]	2,3,7,8-TCDF	Total TCDF[a]
1	Stack Particulate	2.1	79 (9)	NA[b]	62 (27)
	Stack Gas	0.3	4 (9)	NA	17 (15)
	Total (Particulate & Gas)	2.4	83	NA	79
2	Stack Particulate	12.2	142 (11)	NA	27 (26)
	Stack Gas	11.3	228 (12)	NA	1055 (19)
	Total (Particulate & Gas)	23.5	370	NA	1082
3	Stack Particulate	1.9	46 (11)	NA	86 (18)
	Stack Gas	1.7	22 (12)	NA	128 (18)
	Total (Particulate & Gas)	3.6	68	NA	214

(a) The number of TCDD and TCDF isomers found in the samples is shown in parenthesis.

(b) NA - not analyzed.

TABLE 20. TCDD AND TCDF EMISSIONS FROM MASS BURNING UNIT

Test No.	Sample Type	TCDD Concentration, ng/dscm		TCDF Concentration, ng/dscm	
		2,3,7,8-TCDD	Total TCDD[a]	2,3,7,8-TCDF	Total TCDF[a]
1	Stack Particulate	42	167 (4)	27	137 (9)
	Stack Gas (XAD)	20	63 (6)	32	172 (9)
	Total (Particulate & Gas)	62	230	59	309
2	Total (Particulate & Gas)	95	350 (6)	112	577 (9)
3	Total (Particulate & Gas)	33	155 (6)	48	268 (9)

(a) The number of TCDD and TCDF isomers found in the samples is shown in parenthesis.

TABLE 21. TCDD AND TCDF EMISSIONS FROM MODULAR UNIT

Test No.	Sample Type	TCDD Concentration, ng/dscm		TCDF Concentration, ng/dscm	
		2,3,7,8-TCDD	Total TCDD[a]	2,3,7,8-TCDF	Total TCDF[a]
1	Stack Particulate and Stack Gas	0.2	3.3 (9)	NA[b]	18 (15)
2	Stack Particulate	0.05	1.1 (11)	NA	6 (16)
2	Stack Gas	1.5	18 (9)	NA	121 (15)
2	Total (Particulate & Gas)	1.6	19.1	NA	127

(a) The number of TCDD and TCDF isomers found in the samples is shown in parenthesis.

(b) NA - not analyzed.

TABLE 22. ALDEHYDE EMISSION DATA

Unit	Test No.	Concentration in Stack Gas, µg/dscm (ppb)					
		Formaldehyde	Acetaldehyde	Propanal	Acrolein	Pentanal	Benzaldehyde
RDF	1	<5(<4)	1070(580)	340(140)	45(19)		
	2	230(180)	460(250)	54(22)	110(47)		
MASS	1	3280(2630)	1010(550)	110(46)	1230(530)	<6(<2)	1200(270)
	2(Imp 1)	550	130	13	30	<5	3470
	2(Imp 2)	32	10	<5	5	<5	10
	2(Total)	582(466)	140(76)	13(5)	35(15)	<5(<2)	3480(790)
	3	1310(1050)	280(150)	25(10)	70(30)	<6(<2)	230(52)
MOD	1	27(22)	12(7)	<3(<1)	<2(<1)	<6(<2)	460(100)
	2	11(9)	5(3)	<3(<1)	<2(<1)	<6(<2)	810(180)

TABLE 23. ORGANIC COMPOUNDS IDENTIFIED IN RDF PARTICULATE SAMPLES(a)

Tentative Compound Identification(b)	Estimated Concentration in Stack Emissions, $\mu g/m^3$(b)
Compounds in Stack Particulates	
C_2 naphtho(2,3-B)thiophene	12
C_2 alkyl benzene	24
C_2 alkyl benzene	15
C_3 alkyl benzene	2
C_3 alkyl benzene	10
2-ethyl hexanol	10
Tetrachloroethylene	15
C_2 alkyl benzene	7
Diethyl phthalate	7
Dibutyl phthalate	2
Bis(2-ethyl hexyl)phthalate	7
Dichlorobenzene	2
Pentachlorobenzene	2
Tetrachlorobenzene	1
Trichlorobenzene	1

(a) These data provide tentative identities and concentrations of organic compounds which may be present in the stack emissions. The identity of the compounds was not been confirmed. Concentration data may be accurate only to a factor of $\pm$ 5.

(b) From analysis of stack particulate extract only.

TABLE 24. ORGANIC COMPOUNDS IDENTIFIED IN RDF GAS PHASE SAMPLES[a]

Tentative Compound Identification[b]	Estimated Concentration in Stack Emissions, $\mu g/m^3$[b]
Compounds in Gas Phase Samples	
Toluene	37
Tetrachloroethylene	37
C_2 benzene	37
C_2 benzene	22
C_2 benzene	12
Benzaldehyde	17
Phenol	10
Benzofuran	15
Trichlorophenol	12
Chlorobenzene	10
3-pentane-2-one	10
Alkane	10
Methyl pentanol	12
C_2 cyclopentene	12
Hexadecanoic acid	7
Isobenzofurandione/ tetrachlorobenzene	7
Phthalate	7
C_3 alkyl benzene	7
Hydroxybenzaldehyde	6
Benzonitrile	5
Methyl pyrazole	5
Dibenzofuran	3
Chlorostyrene	3

(a) These data provide tentative identities and concentrations of organic compounds which may be present in the stack emissions. The identity of the compounds was not been confirmed. Concentration data may be accurate only to a factor of $\pm$ 5.

(b) From analysis of XAD-2 extract only.

TABLE 25. ORGANIC COMPOUNDS IDENTIFIED IN MASS EMISSION SAMPLES[a]

Tentative Compound Identification[b]	Estimated Concentration in Stack Emissions, $\mu g/m^3$[b]
Styrene	510
Ethyl benzene	260
Benzaldehyde	770
Propynyl benzene	260
Napthalene	2560
Isoquinoline	130
Benzoquinone	130
2-methyl naphthalene	380
1-methyl naphthalene	380
Trichlorophenol	80
Biphenyl	800
Acenaphthalene	1520
1,4-naphthalenedione	130
Dibenzofuran	960
Fluorene	510
9H-fluoren-9-one	130
Anthracene/phenanthrene	1280
1-phenyl napthalene	180
2-phenyl naphthalene	180
Benzo(c)cinnoline	800
Fluoranthene	1280
Pyrene	960
Benzo(g,h,i)fluoranthene	130
Chrysene/Benzo(a)anthracene	60
Benzo(e)pyrene	40
Benzo(a)pyrene	40

(a) These data provide tentative identities and concentrations of organic compounds which may be present in the stack emissions. The identity of the compounds was not been confirmed. Concentration data may be accurate only to a factor of ± 5.

(b) From analysis of combined particulate and XAD-2 sample extracts.

TABLE 26. ORGANIC COMPOUNDS IDENTIFIED IN MOD PARTICULATE SAMPLE[a]

Tentative Compound Identification[b]	Estimated Concentration in Stack Emissions, $\mu g/m^3$[b]
2-chlorophenol	46
Acetophenone	4
Ethyl benzaldehyde	11
$C_{14}H_{36}$	7
Dioctyl adipate	19
Dioctyl phthalate	8

(a) These data provide tentative identities and concentrations of organic compounds which may be present in the stack emissions. The identity of the compounds was not been confirmed. Concentration data may be accurate only to a factor of ± 5.

(b) From analysis of stack particulate extract only.

TABLE 27. VOLATILE HYDROCARBON EMISSION DATA--
MASS BURNING UNIT

Compound	Sample No. 1	Sample No. 2	Sample No. 3
	Concentration in Samples, $\mu g/m^3$		
Chloroform	44	163	248
1,2 Dichloroethane	9,287	9,572	19,000
Tetrachloroethylene	1,120	861	856
o-Dichlorobenzene	54	41	20
Dichlorobenzene	34	49	319
Hexachloroethane	30	27	45
1,3,5-Trichlorobenzene	6	6	5
1,2,4-Trichlorobenzene	38	41	31
Chlorobenzene	47	58	156
	Concentration in Samples, ppb C		
Isobutane	263	584	160
n-pentane	625	1,030	1,362
Benzene	11,735	16,039	36,831
Toluene	66	92	225
Benzaldehyde	128	591	277
p-ethyl toluene	<50	152	184
1,2,4-Trimethylbenzene	70	136	229
Napthalene	279	663	1,169
m+p xylene	<50	<50	304
Total volatile hydrocarbons	74,000	93,000	54,000

DISCUSSION AND SUMMARY

This study provides a comprehensive set of data which characterizes the emissions from three municipal refuse-to-energy incineration units. A significant feature of the data (and that obtained in similar studies) is the large within- and between-site variations both in the composition of the stack emission and level of individual species and compound classes. Attempts to explain these variations and to generalize regarding the significance of the data are difficult and frequently impossible. Some of the factors that frustrate attempts to formulate a clear interpretation of municipal incinerator emission data are:

- Physical and chemical compositional differences in refuse generated in different cities or regions, during different seasons, and by different collection frequencies and methods.
- Physical and chemical compositional variations in feed due to the complex, non-homogeneous nature of municipal refuse
- Lack of accurate information on feed rate and refuse composition during emission measurements
- Lack of information on process operating parameters, i.e., whether abnormal conditions existed during emission measurements.

In the following sections, the data obtained in this study are discussed and references are given to similar measurements made by other investigators. For the most part, however, supporting information are not available to relate specific features of the emission data to incinerator type or design, process operating conditions, or refuse-feed characteristics. Additional studies are required to obtain more detailed information on process-emission relationships.

Physical Characteristics

The particulate mass concentration measured in all Method 5 tests of the RDF and MASS units exceeded the current New Source Performance Standards (NSPS) for municipal incinerators (180 mg/dscm, corrected to 12 percent CO_2). One of the three Method 5 measurements on the MOD unit exceeded the NSPS. A summary of particulate emission data by O'Connell (19) indicates that with a few exceptions, most incinerators are able to meet the NSPS requirements. Data obtained on the Braintree incinerator (20) shows high particulate concentrations which are presumed to result from abnormal combustion conditions.

The size of the particulate material emitted from the RDF and MASS units was also larger than expected for units equipped with electrostatic precipitators. The size distribution and high mass emission levels suggest abnormal combustion and/or ESP operating conditions during the test periods. Visual examination of the particulate catches revealed the presence of large, partially burned chunks of refuse. The carbon content of the RDF and MASS particulate material was also quite high (7 to 32 percent by weight), thus indicating incomplete combustion of the refuse. Particulate size, mass concentrations, and visual examinations indicated that the combustion of refuse in the MOD unit were more efficient.

Chemical Characteristic

The chemical composition of municipal refuse incinerator emissions is dominated by chlorine compounds resulting from combustion of polyvinyl chloride in the refuse. On the average, PVC and other plastics comprise a few percent of municipal refuse composition. Sulfur emitted primarily as SO_2 and inorganic sulfates represents the other major influence on the chemical nature of the emissions. The particulate emissions contain a number of elements such as Zn, Pb, Sn, Sb, Ti, Br, P, Ba, and Cd which, for example, are generally present at levels higher than observed for coal combustion (21).

The particulate emissions from the RDF, MASS, and MOD units was found to have approximately the same elemental composition. The compositions are, also, generally similar to data for incinerators reported by other investigators (20,22,23,24). The elements unique to incinerator emissions that are most likely to impact on the environment include Zn, Sb, Sn, Ti, Cd, and Br.

Mercury was found to be the most abundant volatile trace element in the gaseous emission from all three incinerator units. One very high value (6250 µg/dscm) was obtained for the MASS unit. Nothing abnormal occurred during the collection and analysis of this sample, therefore, the data are presumed to result from an unusually high content of Hg in the refuse feed. Except for one MASS test showing 42 µg/dscm Sb, the concentrations of As, Se, Sb, and Pb were determined to be <10 µg/dscm.

Based on the anion analyses and FT-IR speciation, the principal inorganic compounds in the particulate emissions are chlorides and sulfates. Carbonates were also identified by FT-IR as a possible component of the particulate emissions. Specifically, the FT-IR work noted the lack of oxides in the particulate emissions.

The levels of HCl detected in the RDF and MASS unit were in approximately the same range; 352 to 516 mg/dscm (232 to 340 ppm). Lower values (35-153 ppm) were found in the MOD emissions. Other investigators (20,25,26,27,28,29) report HCl emission levels which are generally lower than the RDF and MASS values. Gaseous HF emission concentrations are lower than values for other incinerator units summarized by O'Connell (19).

In general, the levels of organic compounds found in the RDF, MASS, and MOD emissions varied widely. Most notable are the PAH levels which span approximately three orders of magnitude. The highest total PAH concentrations found in the RDF and MOD emissions were approximately 15 and 18 µg/dscm, respectively. The highest total PAH concentration measured in the MASS emissions was approximately 12 mg/dscm. Lower molecular weight PAH compounds (naphthalenes, anthracene) were present in the highest concentrations, in emissions of the three units, however, higher molecular weight compounds (benzopyrenes) were found in the MASS emission samples. The PAH emisson levels determined in this study appear to be higher than data reported by other investigators (20,30,31,32). However, it is difficult to compare the results because in some cases only data for the particulate emissions were reported.

The average levels of total TCDD and TCDF observed in the emissions of the three units ranged from 11 to 245 ng/dscm and 73 to 458 ng/dscm, respectively. Higher TCDD and TCDF values were measured in the RDF and MASS emissions. The emission data obtained in this study fall within the rather broad range of values reported by other researchers (33-61). (The extensive number of references for dioxins and furans reflects the widespread attention that has been given to their measurement in incinerator and other source emissions.) O'Connell (62) in summarizing the data from these references reports extremes of 0.3 to 10,536 ng/dscm of total TCDD in incinerator emissions (particulate and vapor phases combined). The average and median of total TCDD emission values (particulate and vapor phases) reported in the literature is 243 and 24 ng/dscm, respectively. On the average, 77 percent of the total TCDD was found in the gaseous phase of the emissions. However, TCDD was found predominately in the particulate phase in measurements performed during this study.

The aldehyde levels observed in this study are in approximately the same range as reported for the Braintree unit (20). Total aldehyde levels were found to be the highest in the stack emissions of the MASS unit and the lowest in the MOD emissions. The range in emission concentrations for the three units were as follows: formaldehyde - <5 to 3280 µg/dscm (<4 to 2630 ppb), acetaldehyde - 5 to 1070 µg/dscm (3 to 580 ppb), propanal - <3 to 340 µg/dscm (<1 to 140 ppb), acrolein - <2 to 1230 µg/dscm (<1 to 530 ppb), and benzaldehyde - 230 to 3480 µg/dscm (52 to 790 ppb).

The RDF and MASS emission meausrements showed considerable variation both in total aldehyde concentrations and in the levels of the individual aldehydes observed in replicate tests. The samples for aldehyde measurements were not obtained concurrently with samples for the determination of the other organic compounds, e.g., PAH, TCDD/TCDF, etc. Thus, trends and variations in the aldehyde data cannot directly related to those observed for the other organic compounds.

The GC/MS screening analysis provides the tentative identity and a semiquantitative concentration estimate of other organic compounds in the emissions of the three refuse-to-energy systems. The GC/MS screening results generally show a higher level of organic compounds in the MASS emissions; an observation that is consistent with the relative emission levels of PAH and aldehyde compounds from the three units. Compounds with aromatic structure predominate the composition of the samples from all three units.

The screening or survey data was obtained to provide a preliminary estimate of the types of organic compouncs in refuse-to-energy system emissions. These data must be critically examined to assess whether any of the compounds, at the estimated emission levels, pose a threat to human health and/or the environment. Additional, more specific, measurements should be performed to confirm the presence and to characterize the emission levels of those compounds or compound classes that may cause adverse health or environmental effects. Limited data were also obtained for volatile hydrocarbon emissions (MASS unit only).

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APPENDIX A

INFRARED SPECTRA OF REFUSE-TO-ENERGY INCINERATOR PARTICULATE EMISSION SAMPLES

The infrared spectra of particulate emission samples from the three refuse-to-energy incinerators are present in Figures A-1 through A-18 in this appendix. Spectra of samples from each incinerator unit were obtained for the following sample treatments:

- As-received particulate material
- Water-insoluble fraction of particulate material - baked for 3 hours at 200°C
- Water-insoluble fraction of particulate material - unbaked
- Water-soluble fraction of particulate material - baked for 3 hours at 200°C
- Water-soluble fraction of particulate material - unbaked.

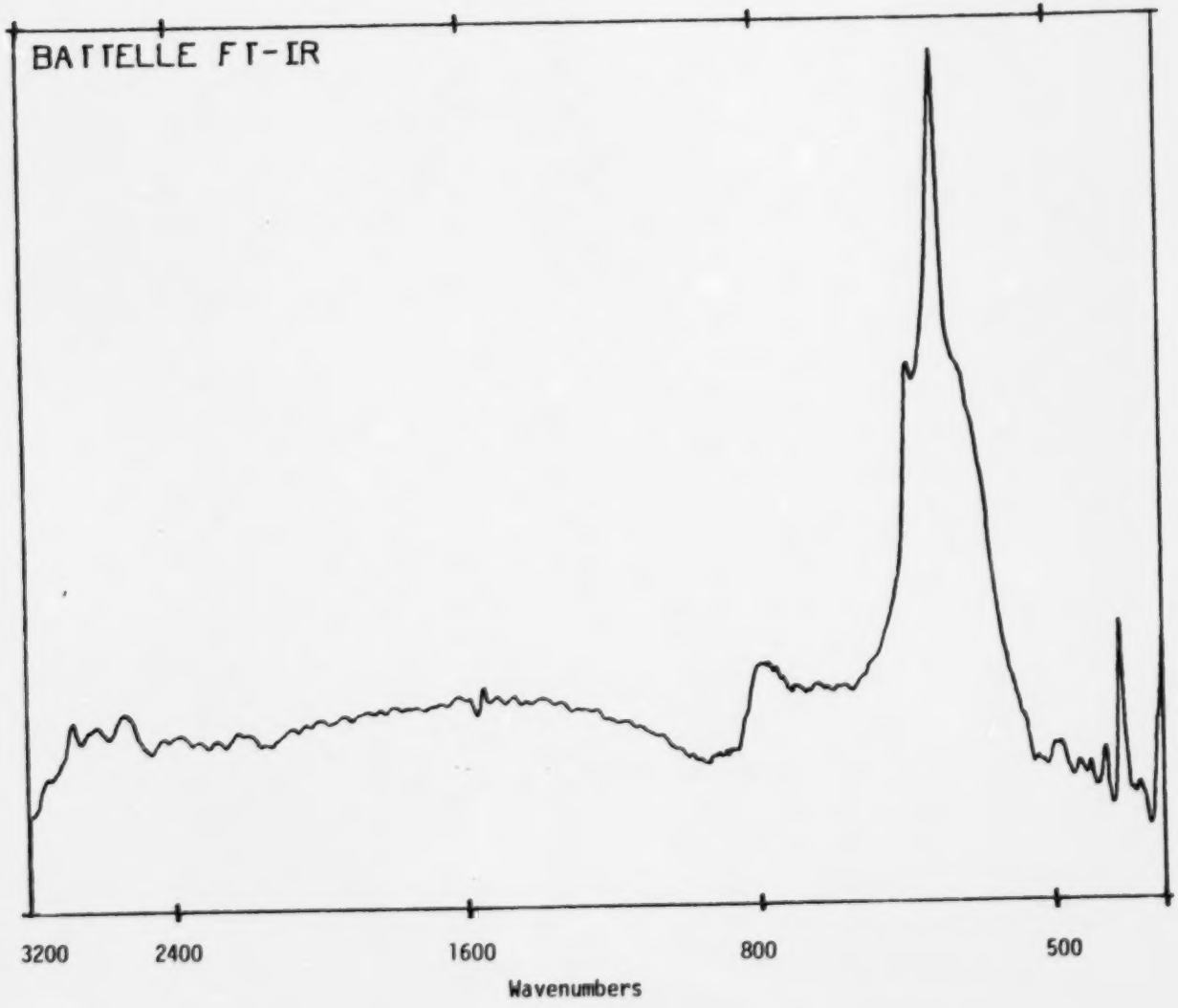


Figure A-1. As received RDF sample.

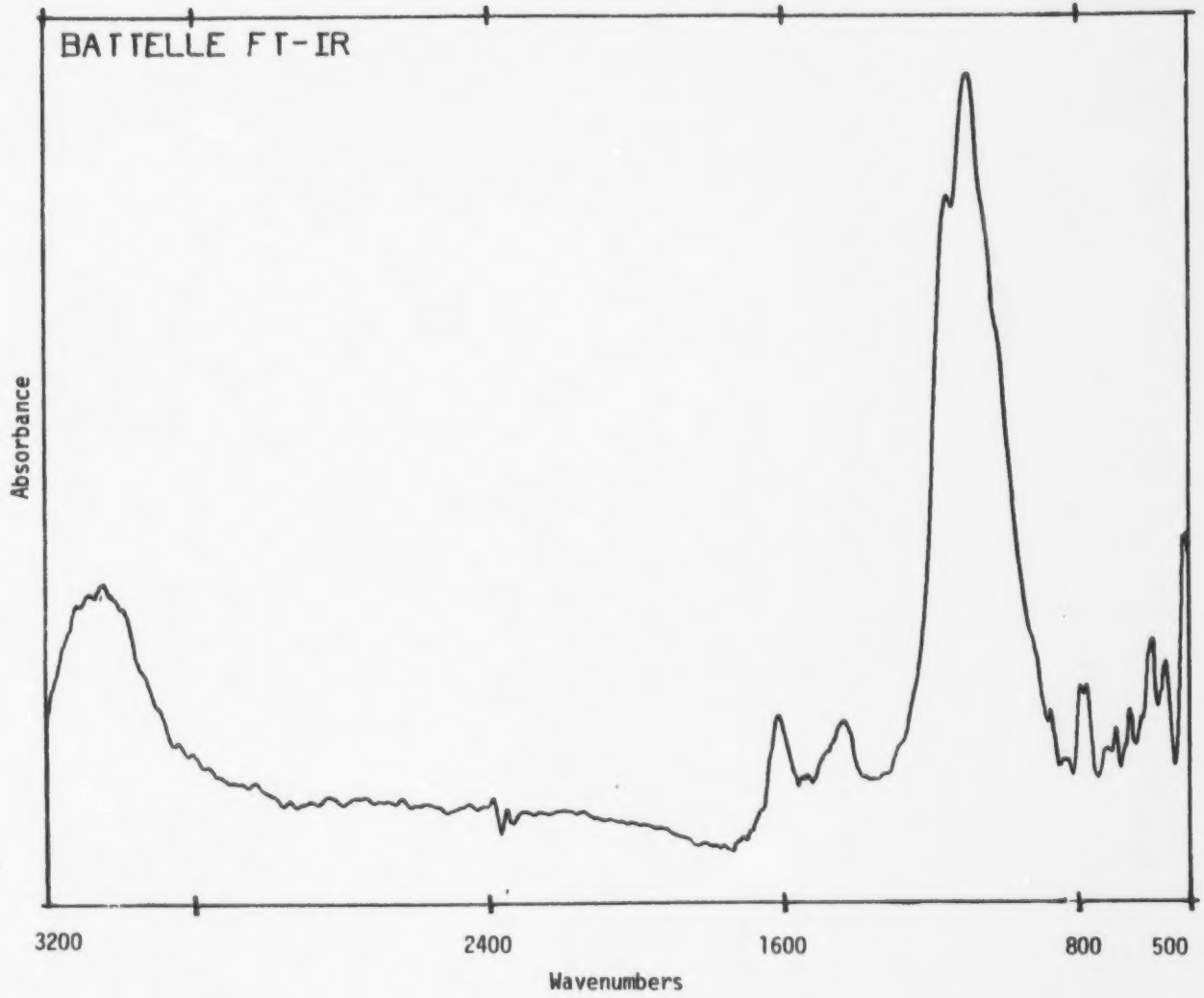


Figure A-2. As received MASS sample.

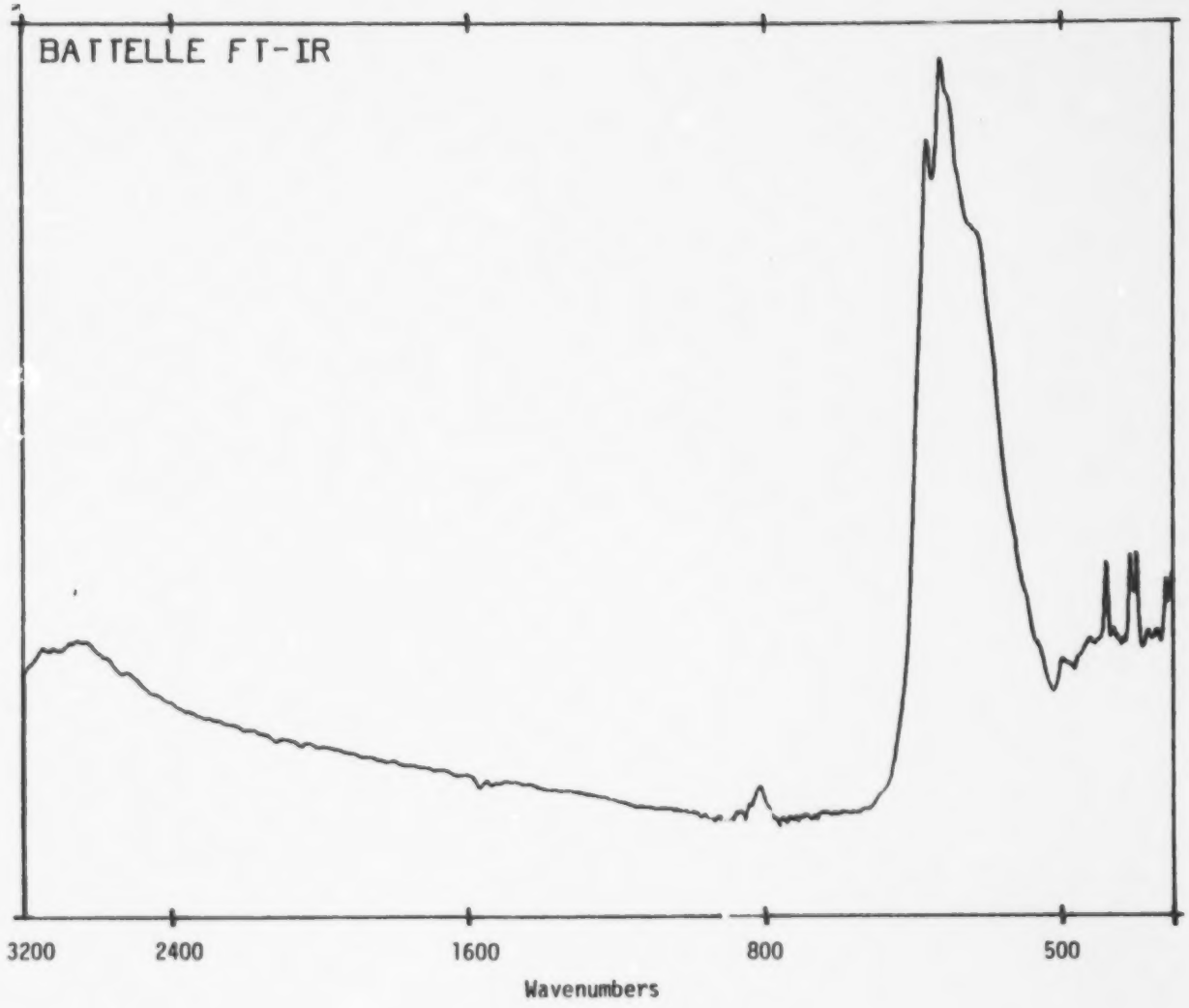


Figure A-3. As received MOD sample.

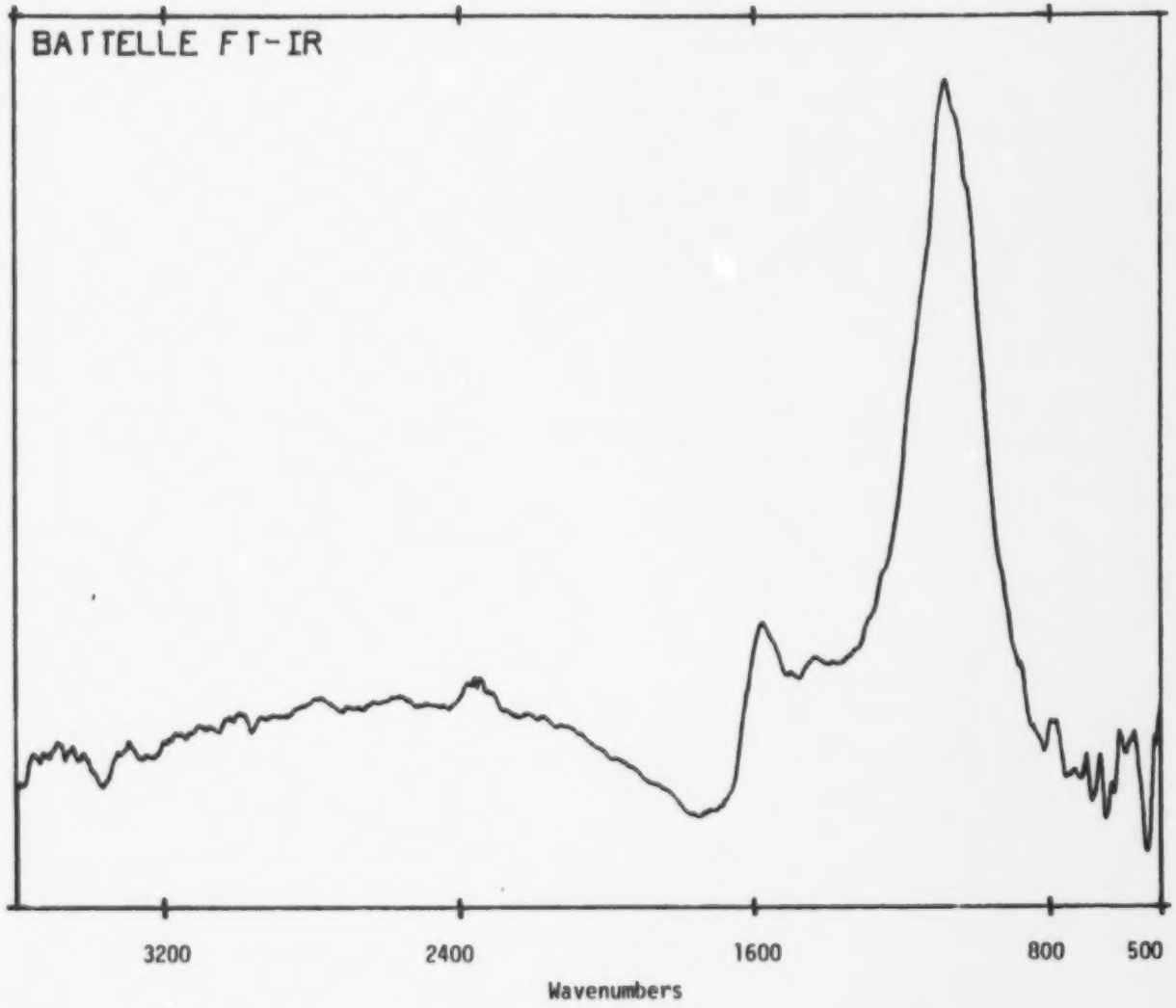


Figure A-4. RDF water-insoluble fraction, unbaked.

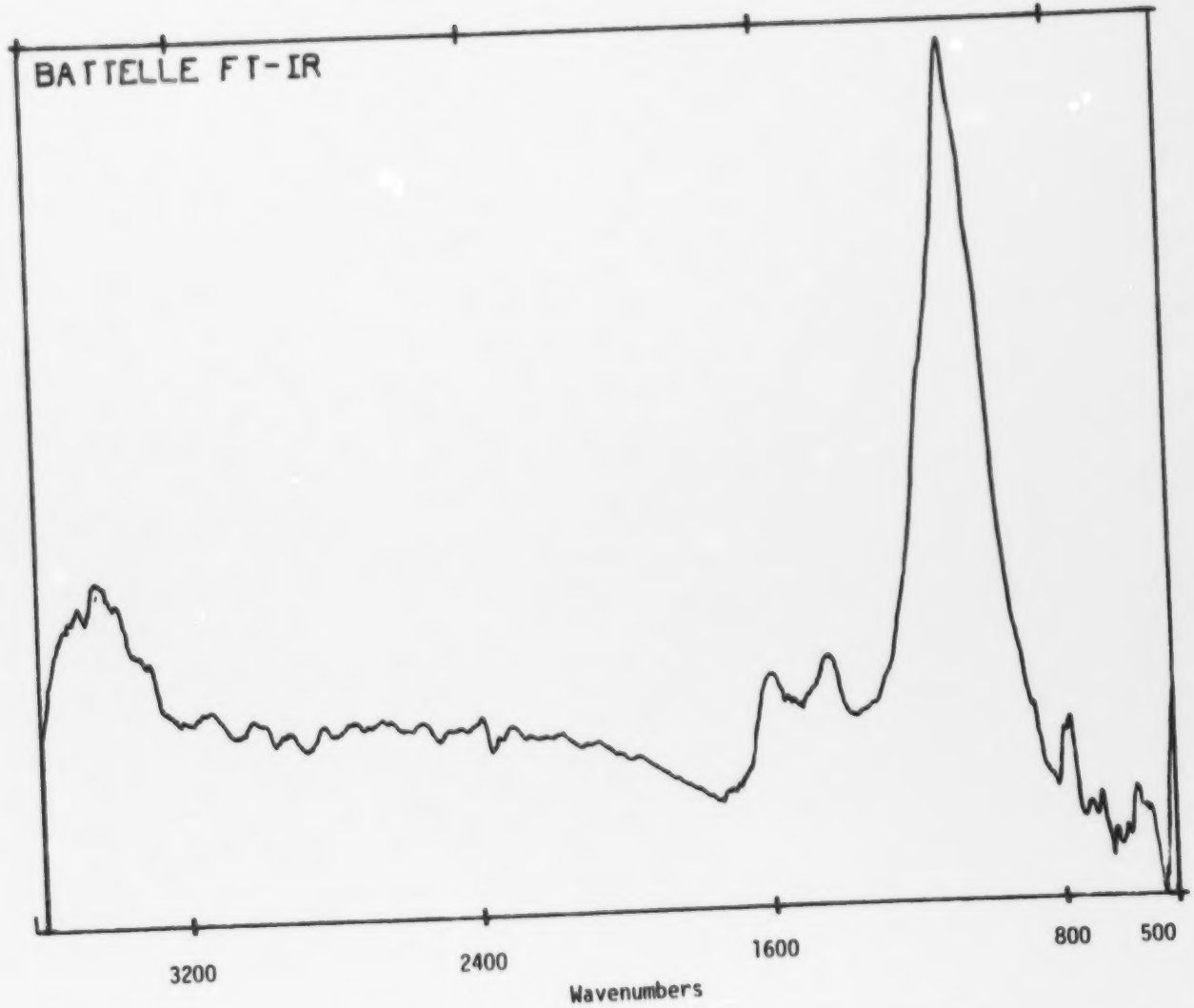


Figure A-5. MASS water-insoluble fraction, unbaked.

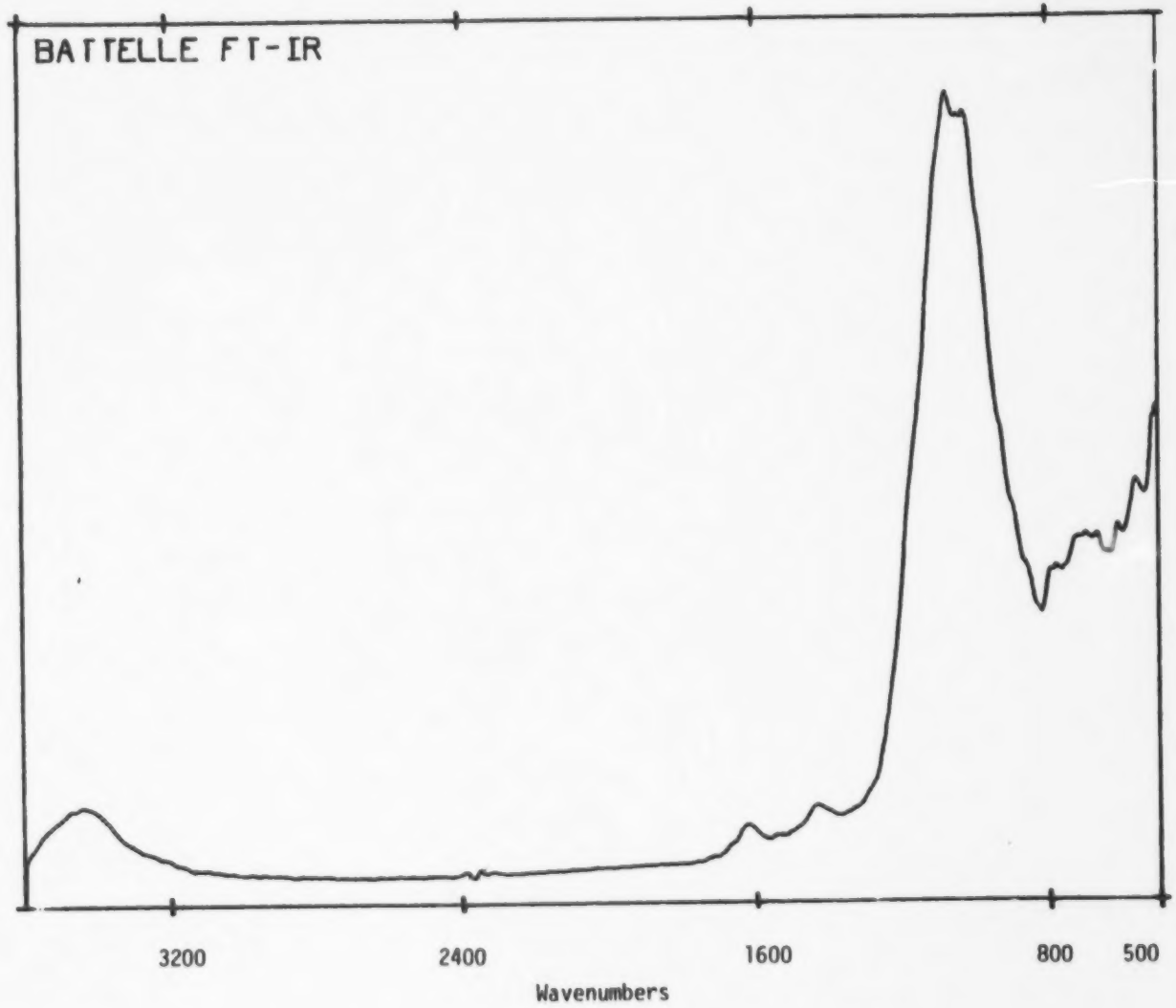


Figure A-6. MOD water-insoluble fraction, unbaked.

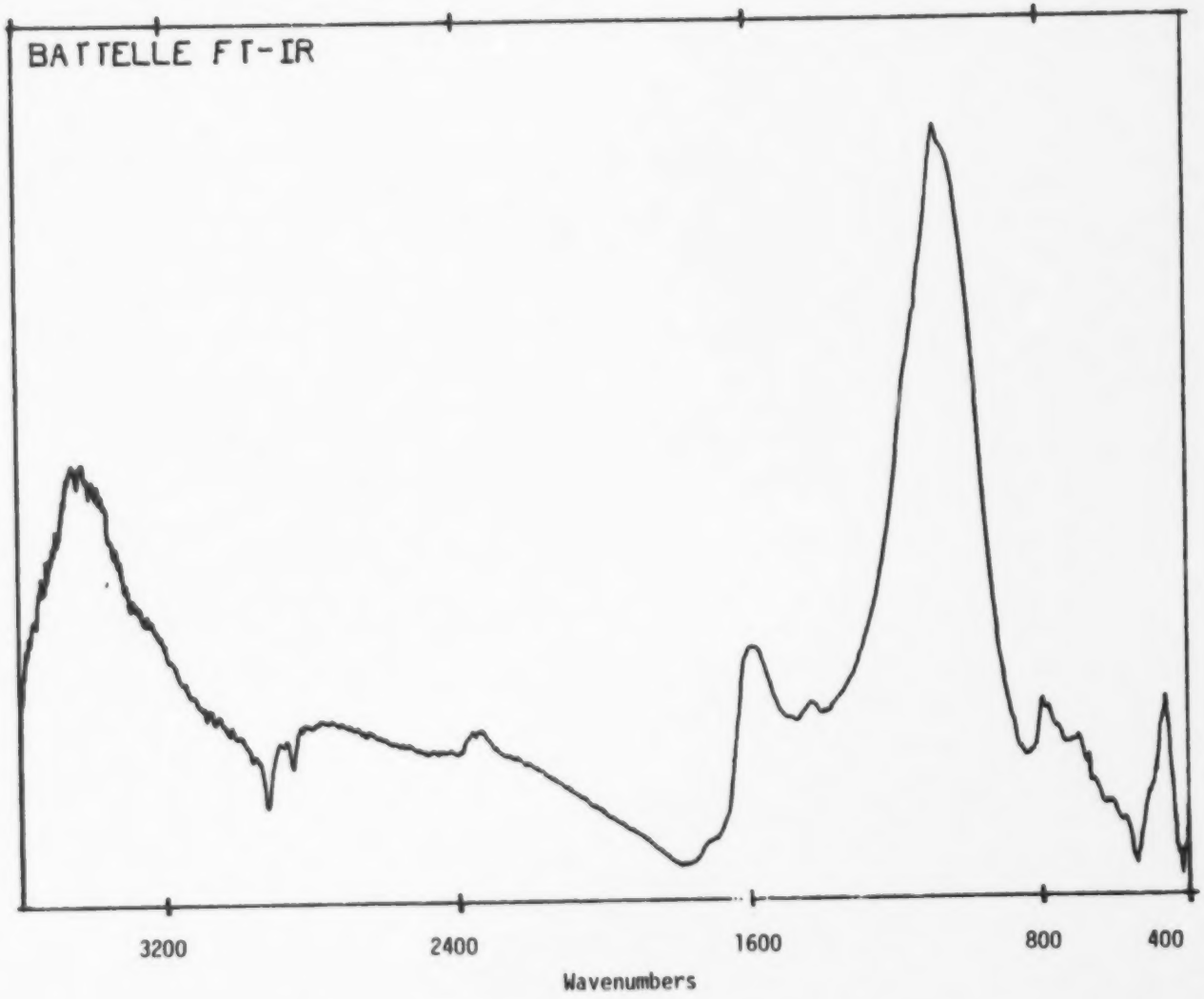


Figure A-7. RDF water-insoluble fraction, baked.

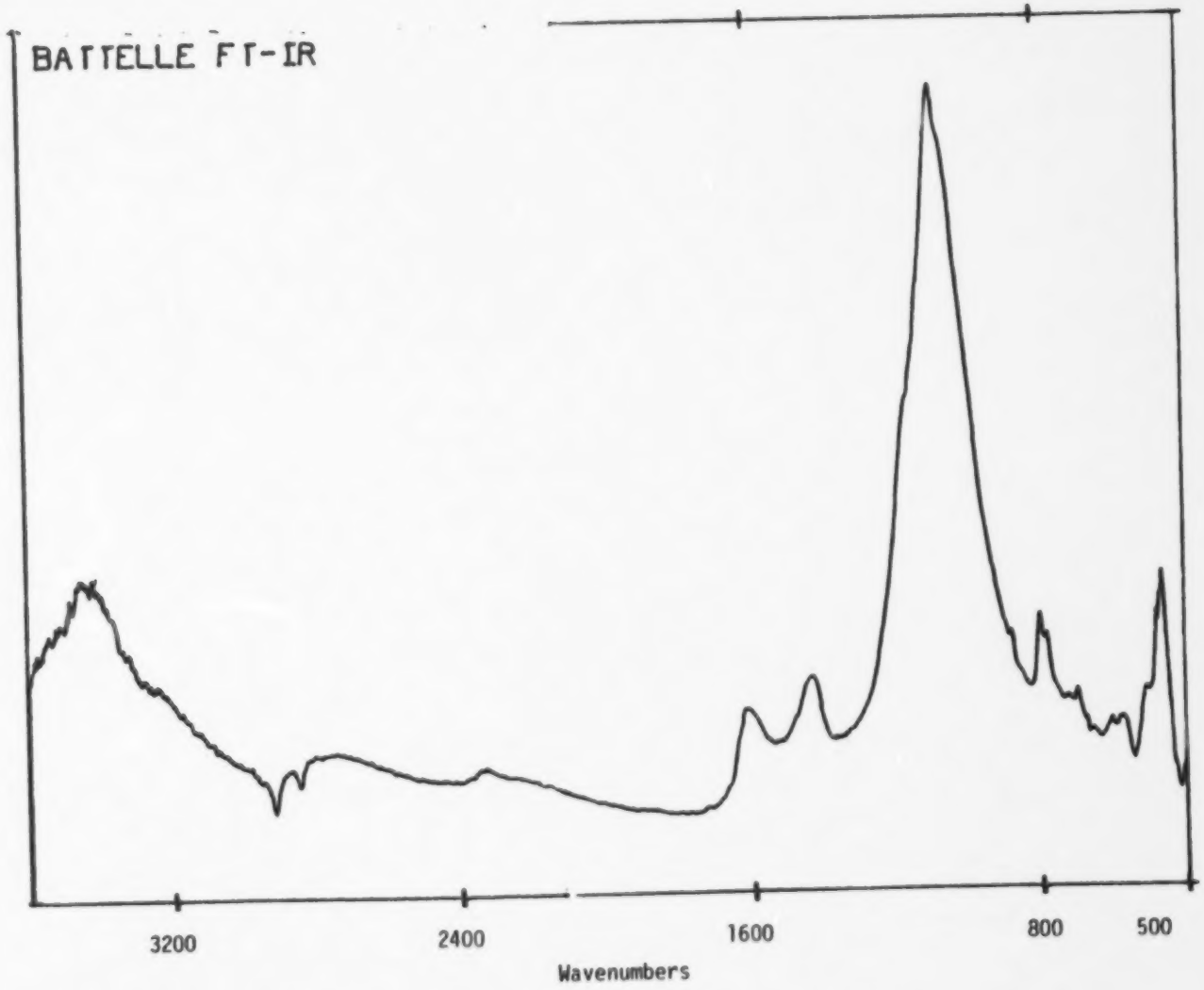


Figure A-8. MASS water-insoluble fraction, baked.

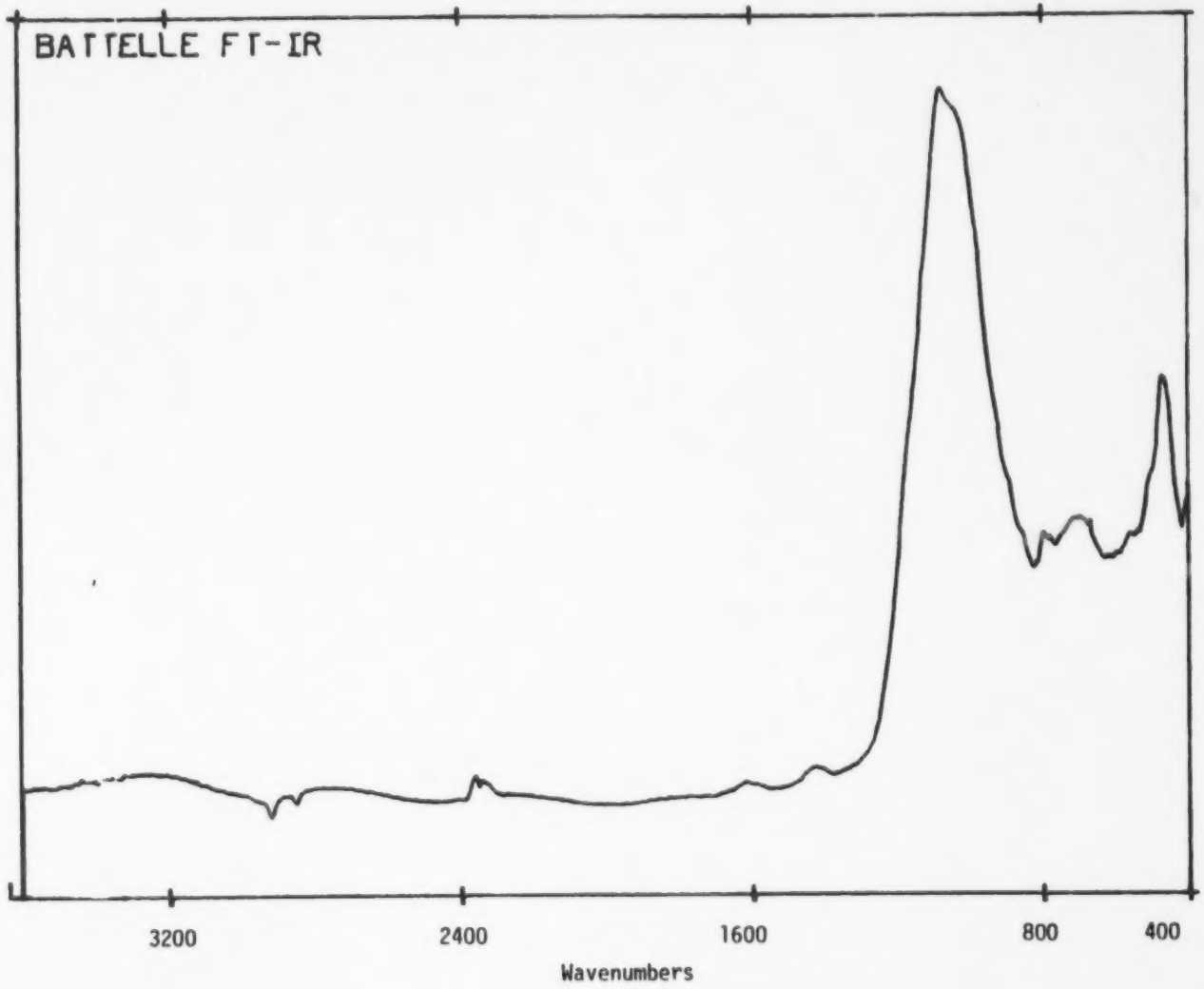


Figure A-9. MOD water-insoluble fraction, baked.

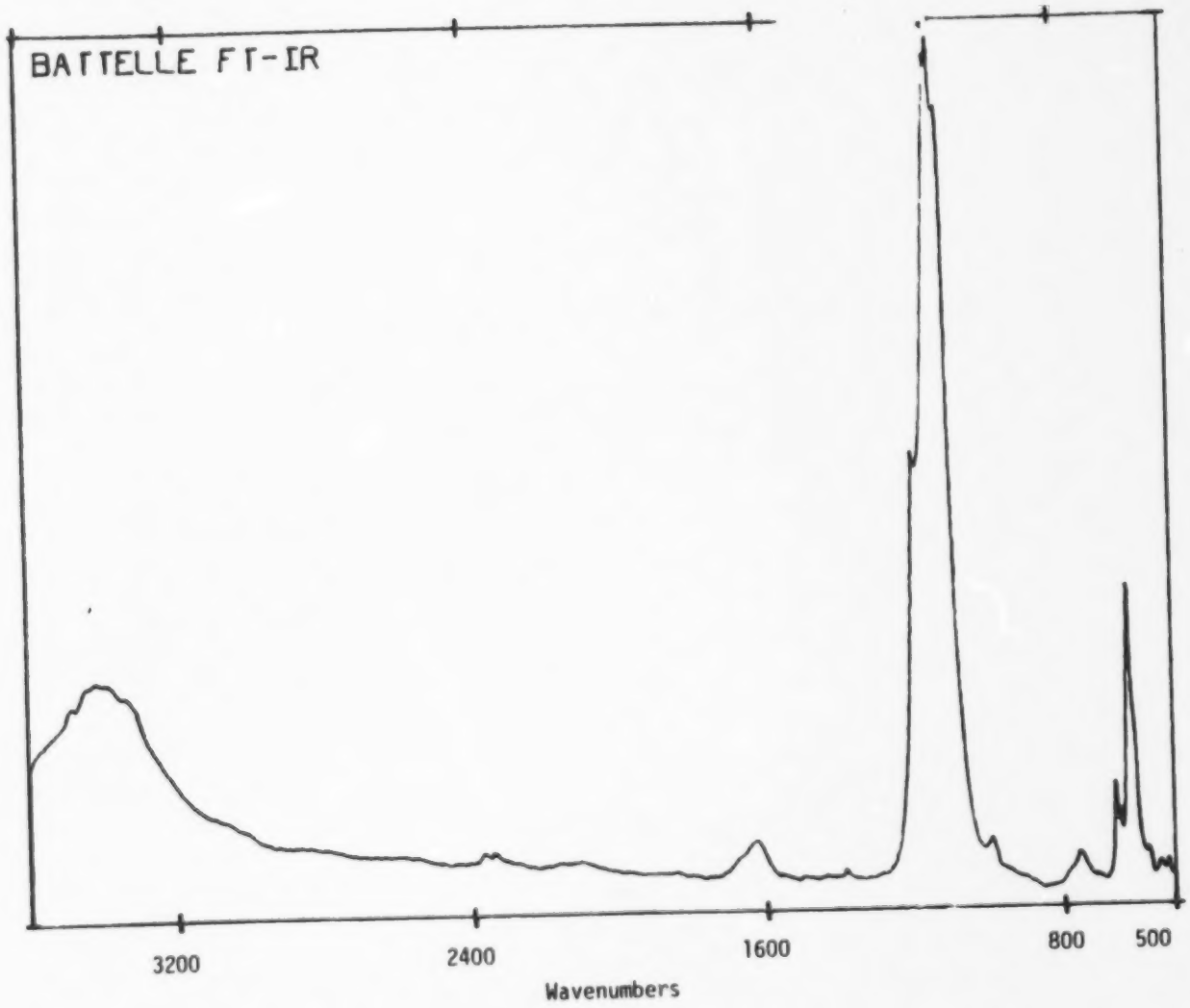


Figure A-10. RDF water-soluble fraction, unbaked.

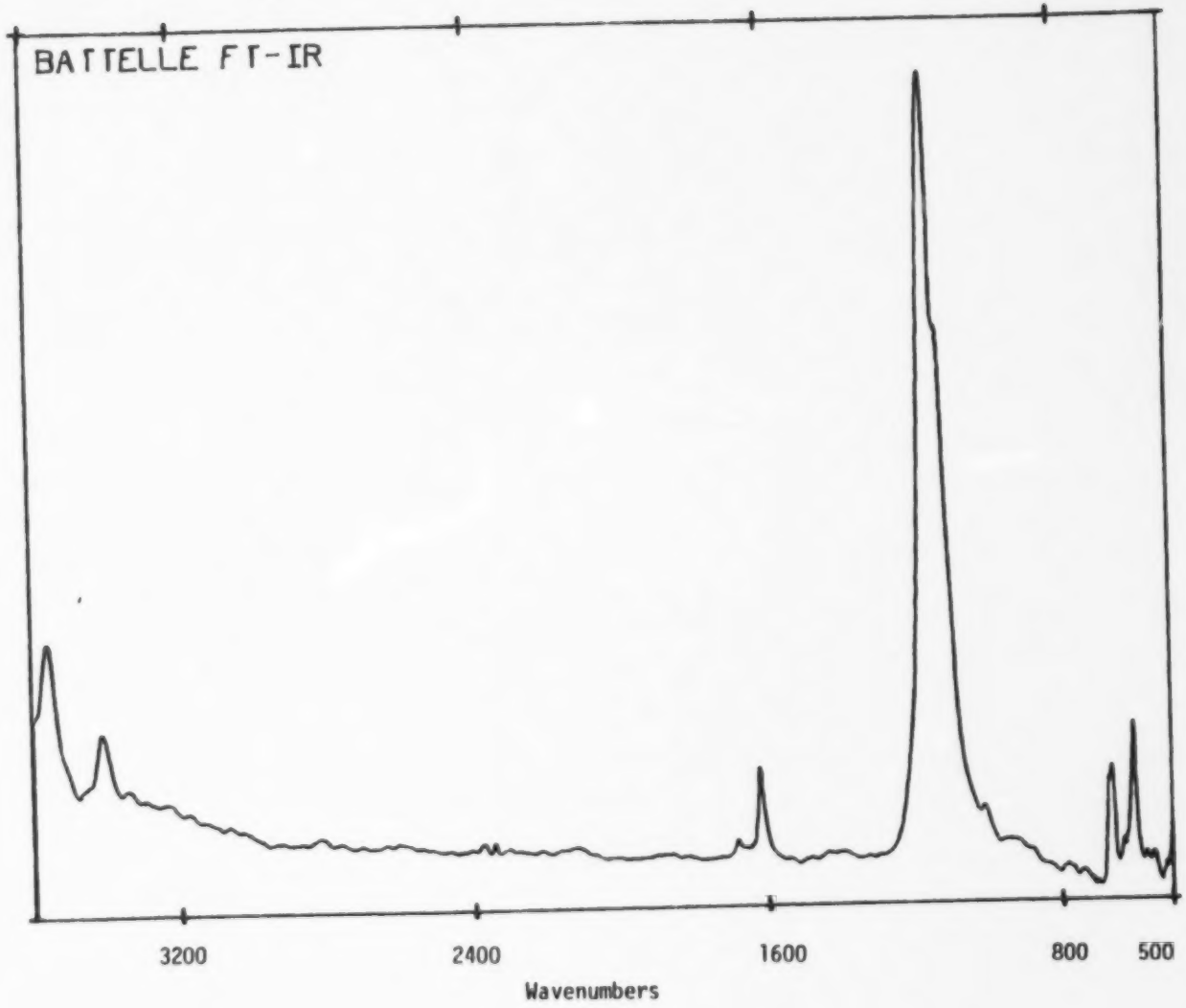


Figure A-11. MASS water-soluble fraction, unbaked.

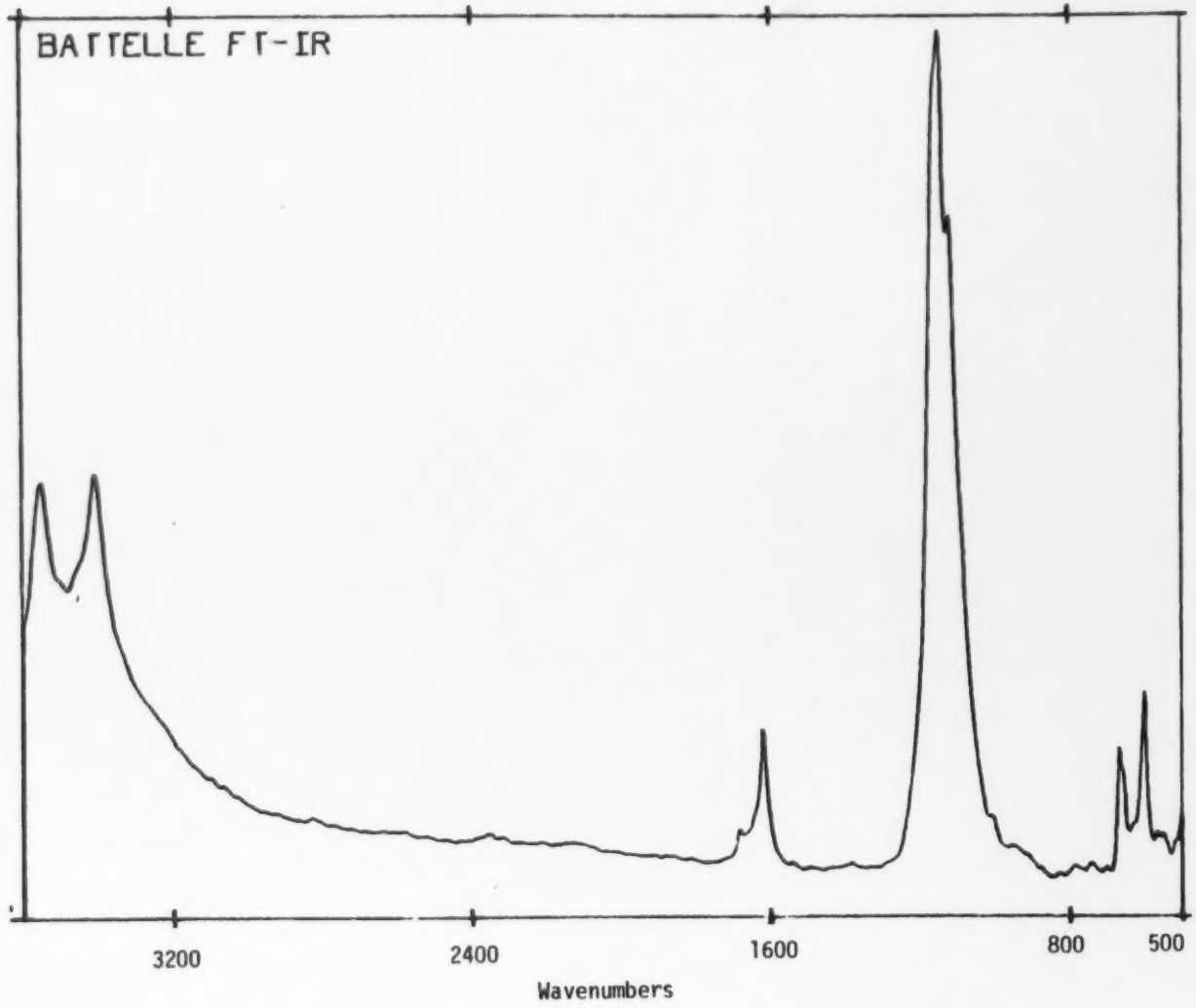


Figure A-12. MOD water-soluble fraction, unbaked.

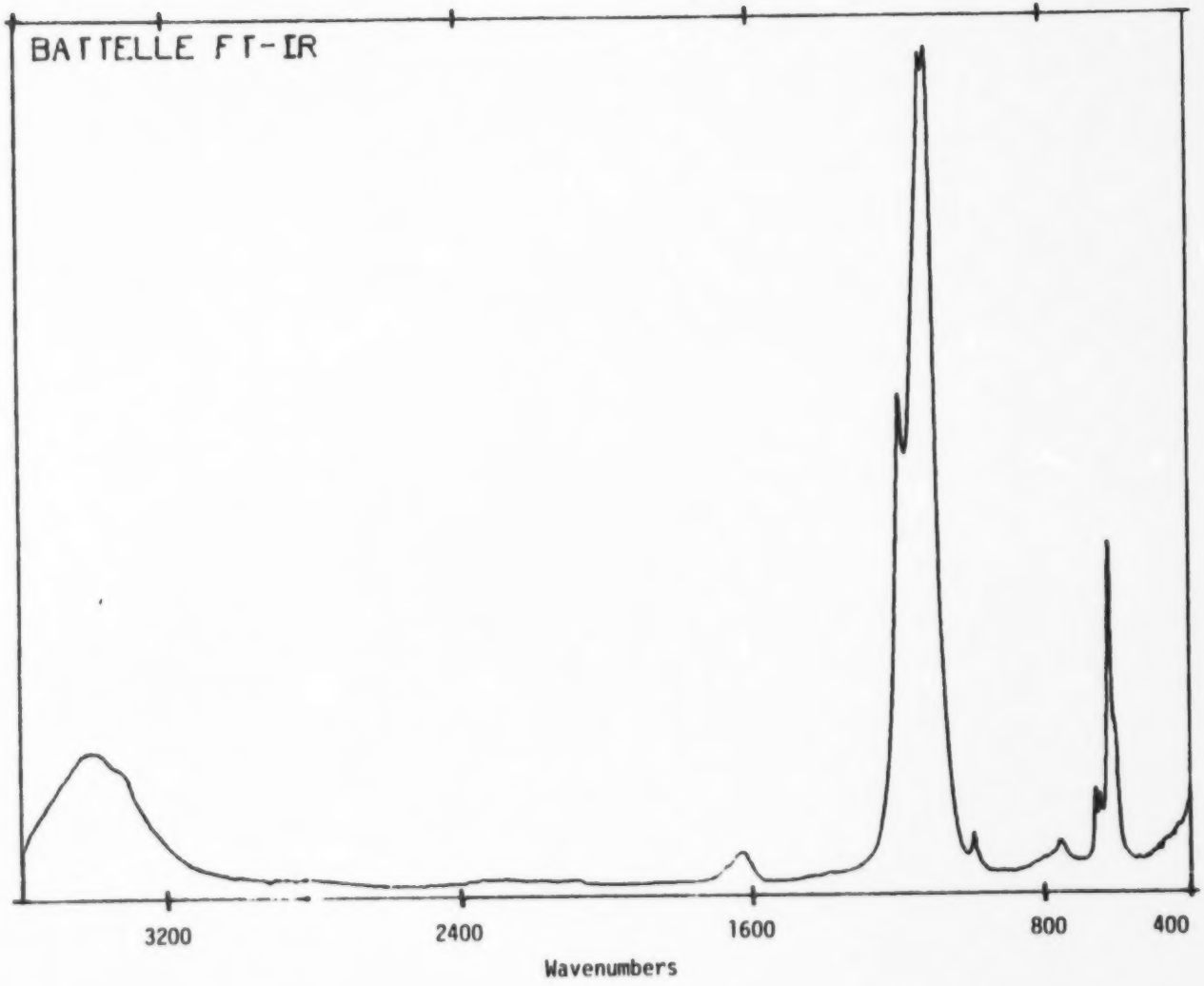


Figure A-13. RDF water-soluble fraction, baked.

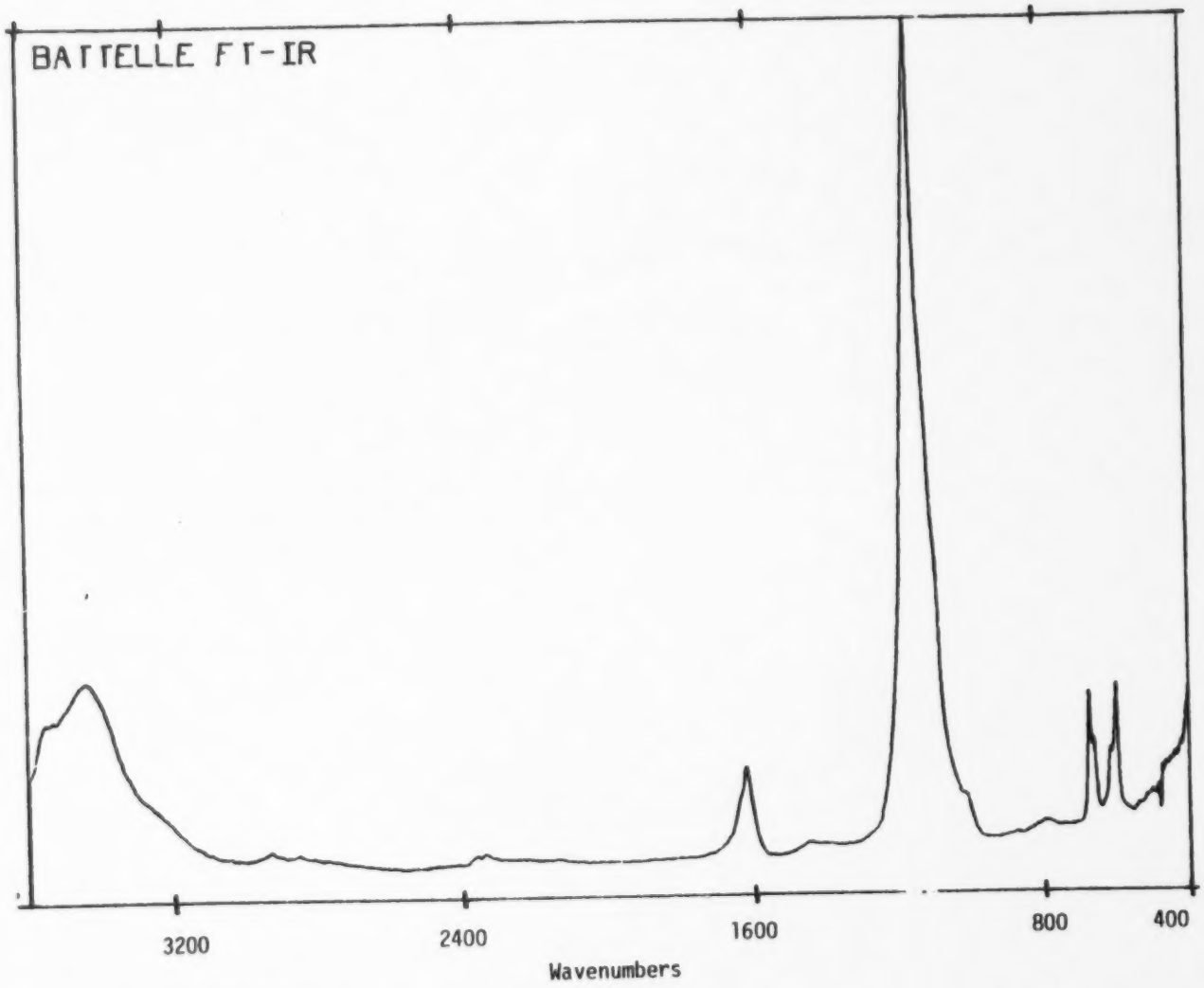


Figure A-14. MASS water-soluble fraction, baked.

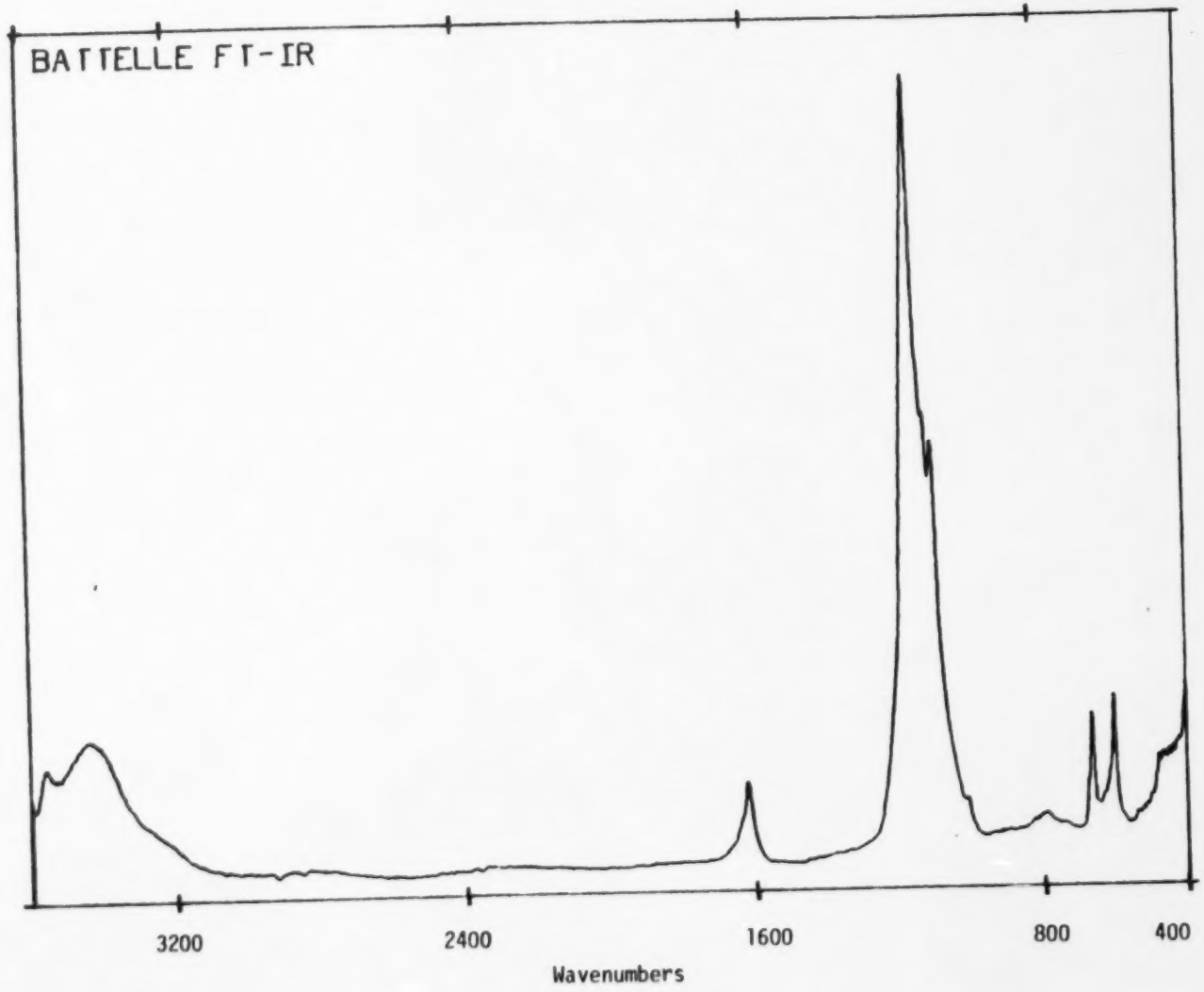


Figure A-15. MOD water-soluble fraction, baked.

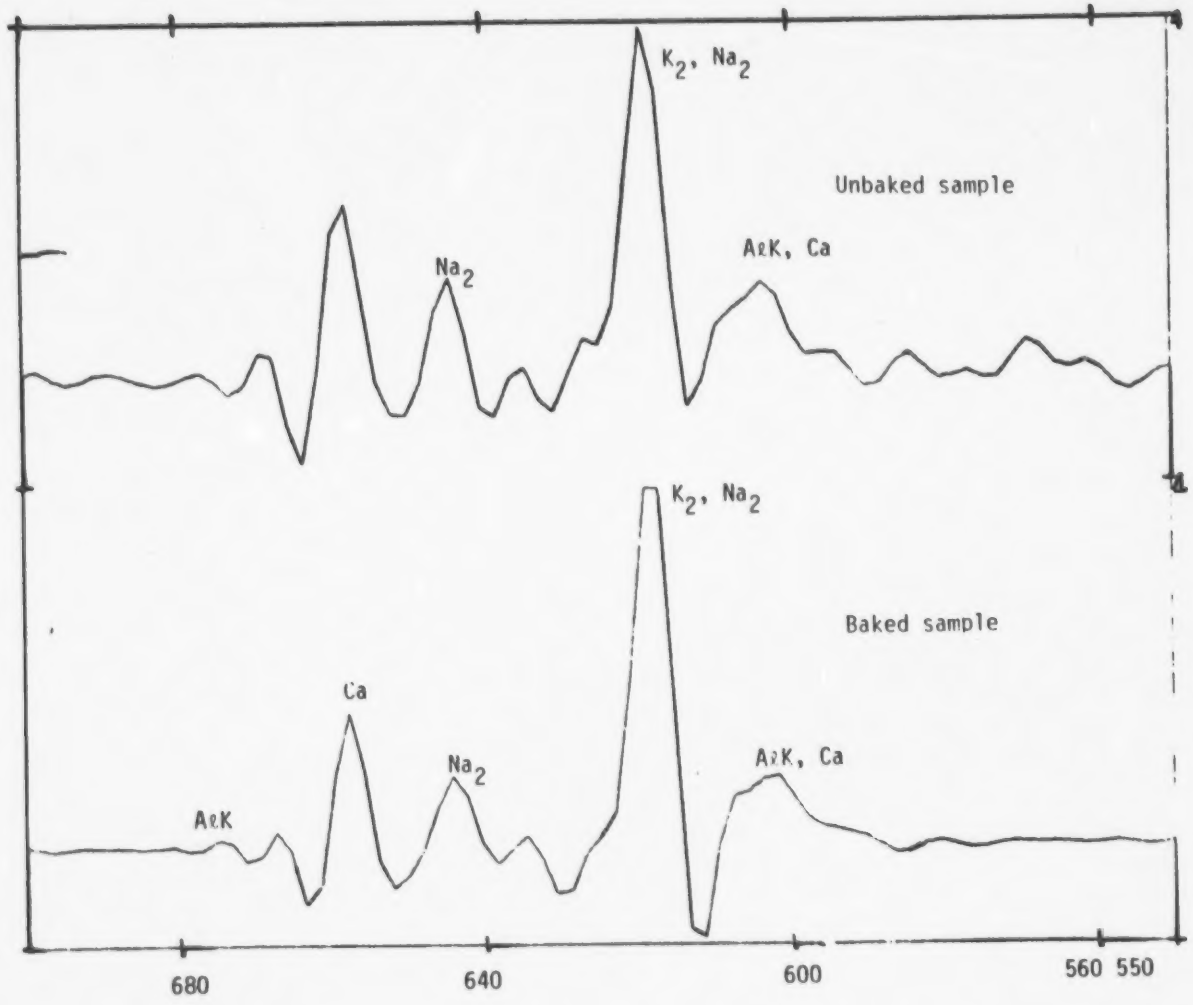


Figure A-16. Deconvoluted spectra of RDF water-soluble fraction.

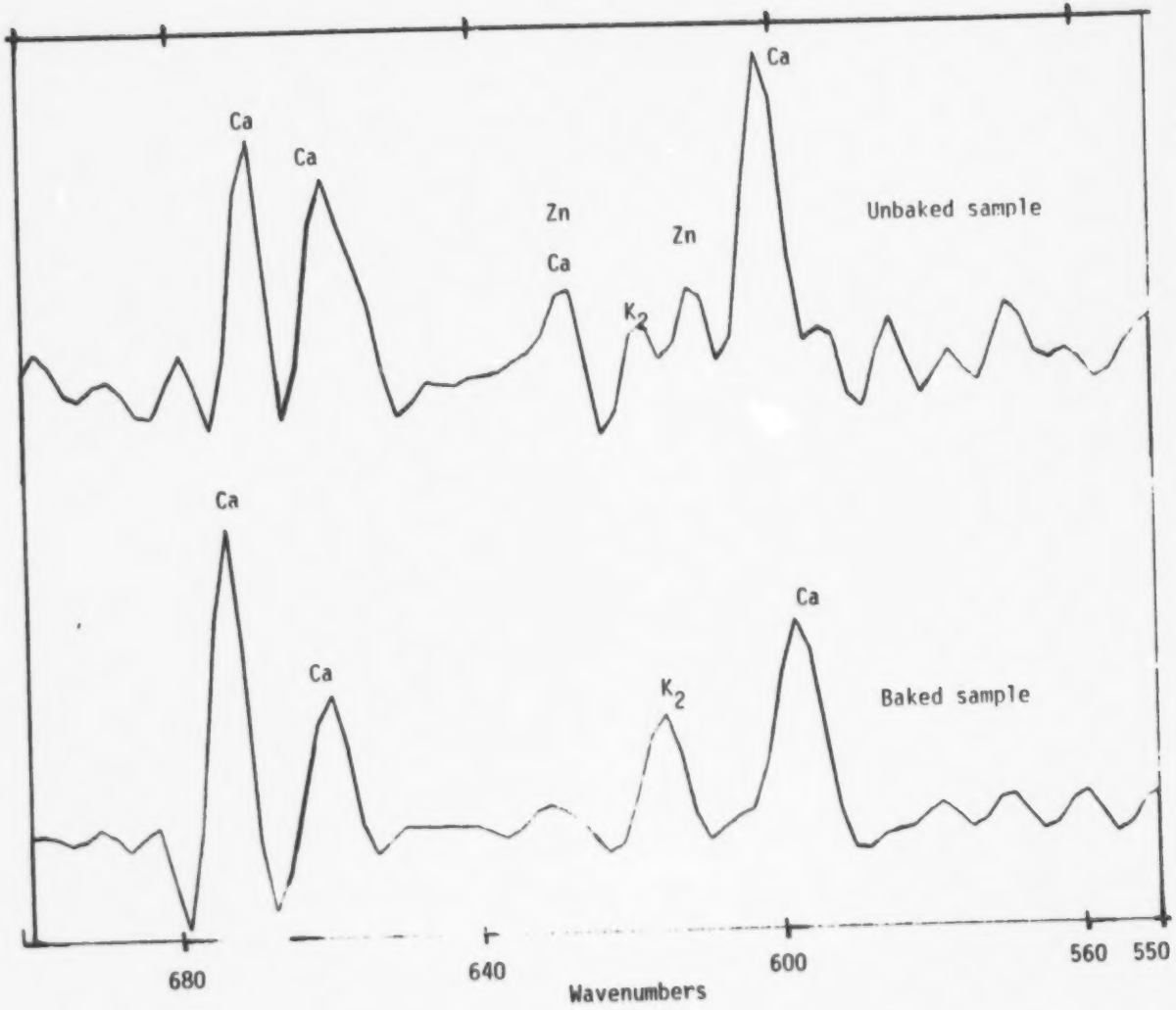


Figure A-17. Deconvoluted spectra of MASS water-soluble fraction.

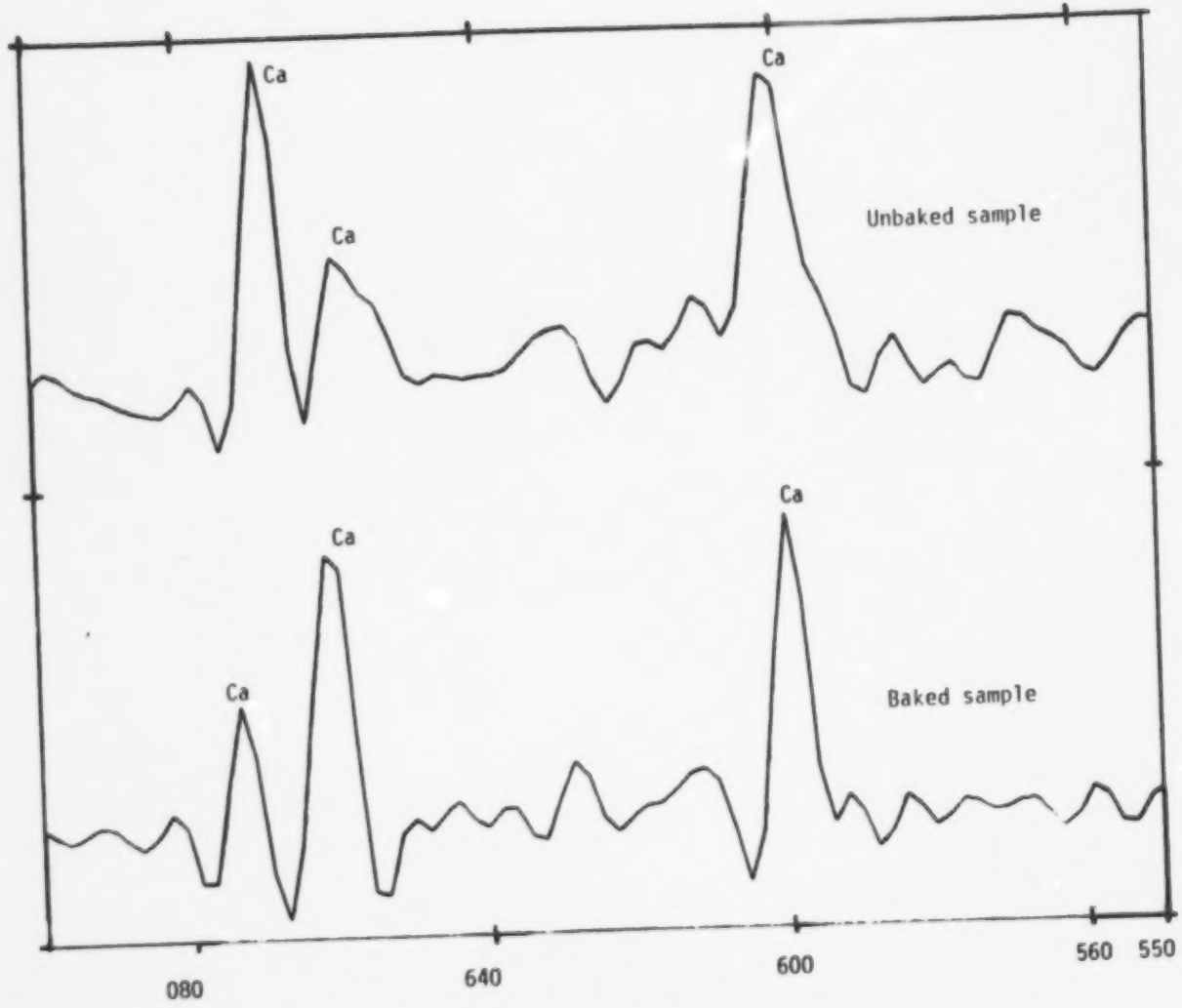


Figure A-18. Deconvoluted spectra of MOD water-soluble fraction.

APPENDIX B

TCDD/TCDF SELECTED ION CURRENT PROFILES

This appendix presents high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) selected ion current profiles which are representative of the particulate and gas phase emission samples collected at the three refuse-to-energy incinerator sites. The data for each sample is comprised of three selected ion current traces: (a) M/Z 304 and 306 - TCDF isomers, (b) M/Z 320 and 322 - TCDD isomers, and (c) M/Z 332 and 334 -2,3,7,8-TCDD-$^{13}C_{12}$ internal standard. It should be noted that the same vertical scale (peak height) setting was not used for all the selected ion current traces.

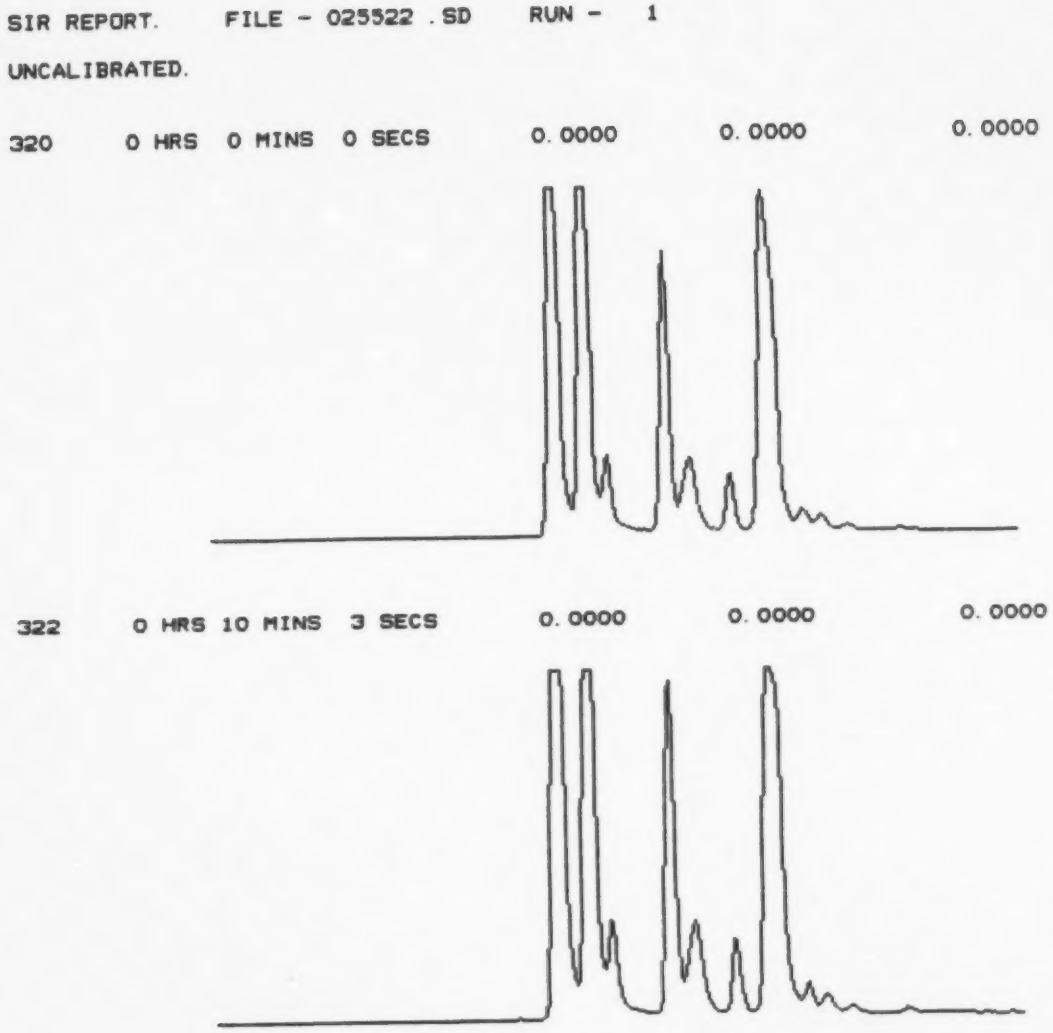
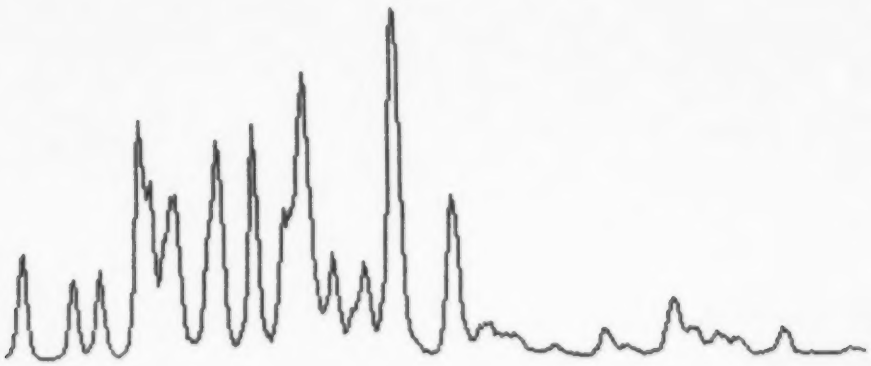

SIR REPORT. FILE - 025522 .SD RUN - 1
UNCALIBRATED.
320 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
322 0 HRS 10 MINS 3 SECS 0.0000 0.0000 0.0000
RDF Stack Particulate Sample
Mod. Method 5 Test No. 2

Figure B-1. Typical selected ion current profile for TCDD.

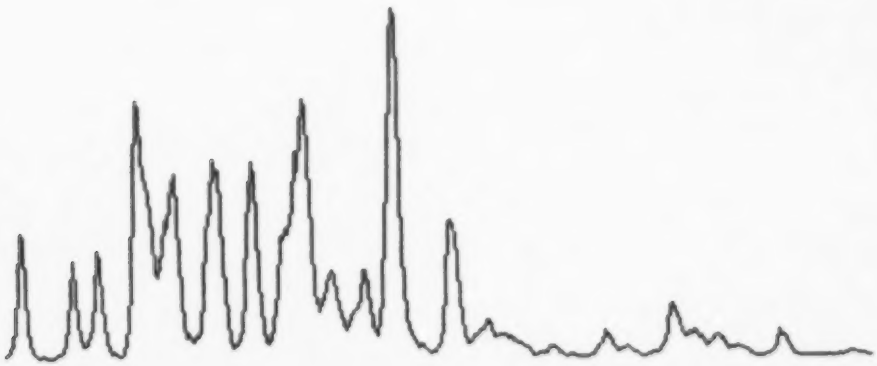
SIR REPORT. FILE - TCDDF2 .SD RUN - 1

UNCALIBRATED.

304 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000



306 0 HRS 0 MINS 3 SECS 0.0000 0.0000 0.0000



RDF Stack Particulate Sample
Mod. Method 5 Test No. 2

Figure B-2. Typical selected ion current profile for TCDF.

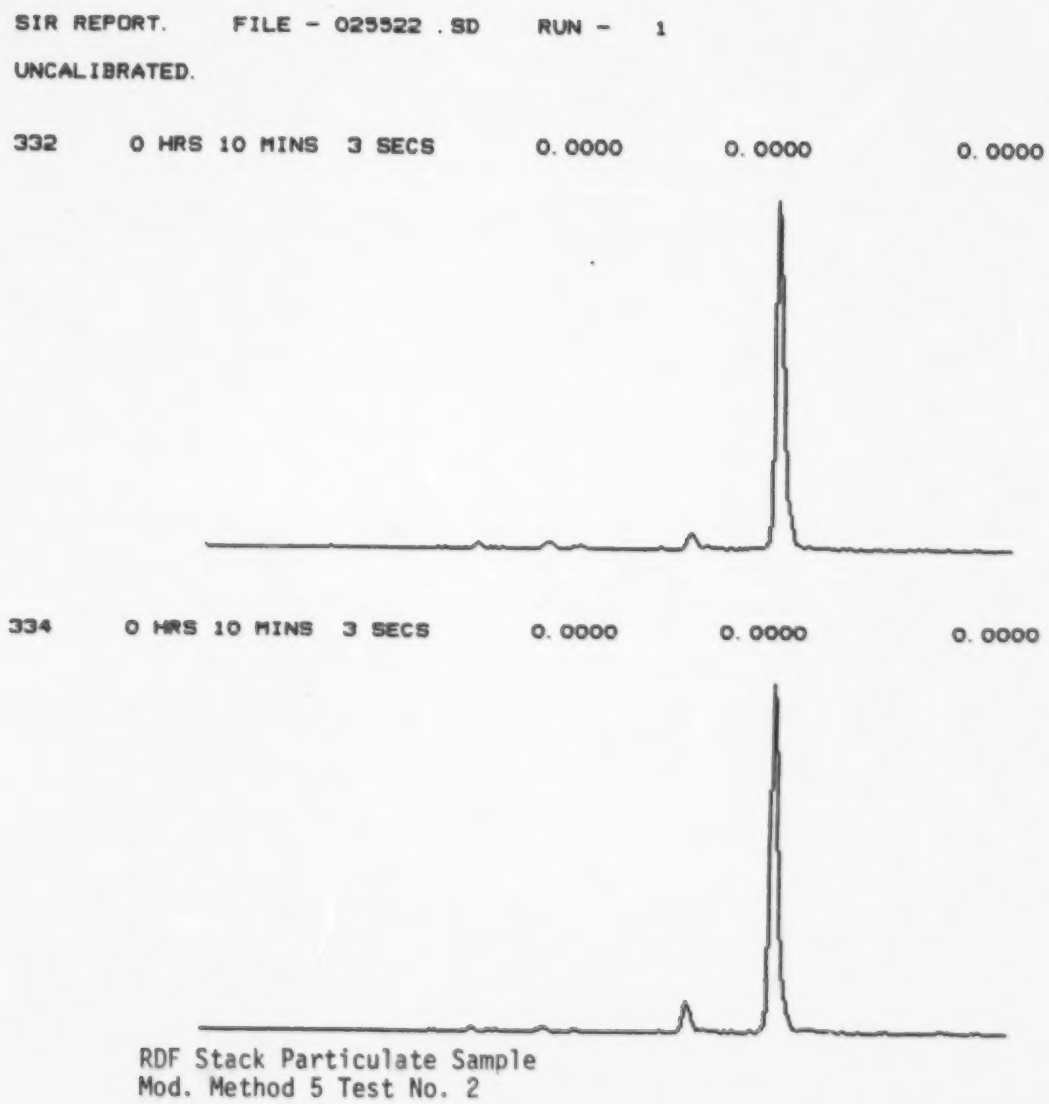
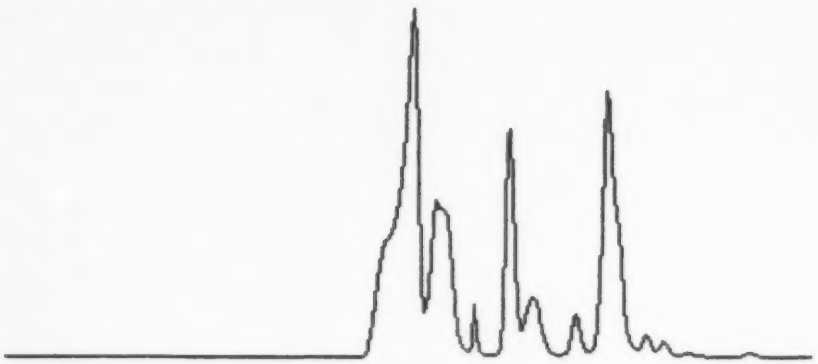

SIR REPORT. FILE - 025522 .SD RUN - 1
UNCALIBRATED.
332 0 HRS 10 MINS 3 SECS 0.0000 0.0000 0.0000
334 0 HRS 10 MINS 3 SECS 0.0000 0.0000 0.0000
RDF Stack Particulate Sample
Mod. Method 5 Test No. 2

Figure B-3. Typical selected ion current profile for internal standard.

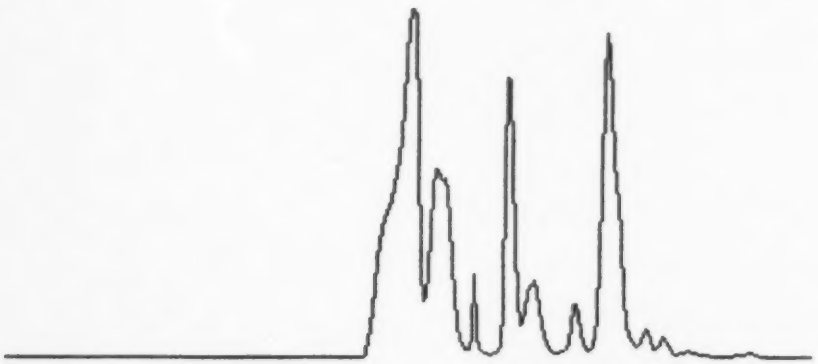
SIR REPORT. FILE - 025528 .SD RUN - 1

UNCALIBRATED.

320 0 HRS 10 MINS 2 SECS 0.0000 0.0000 0.0000



322 0 HRS 10 MINS 3 SECS 0.0000 0.0000 0.0000



RDF Gas Phase Sample
Mod. Method 5 Test No. 2

Figure B-4. Typical ion current profile for TCDD.

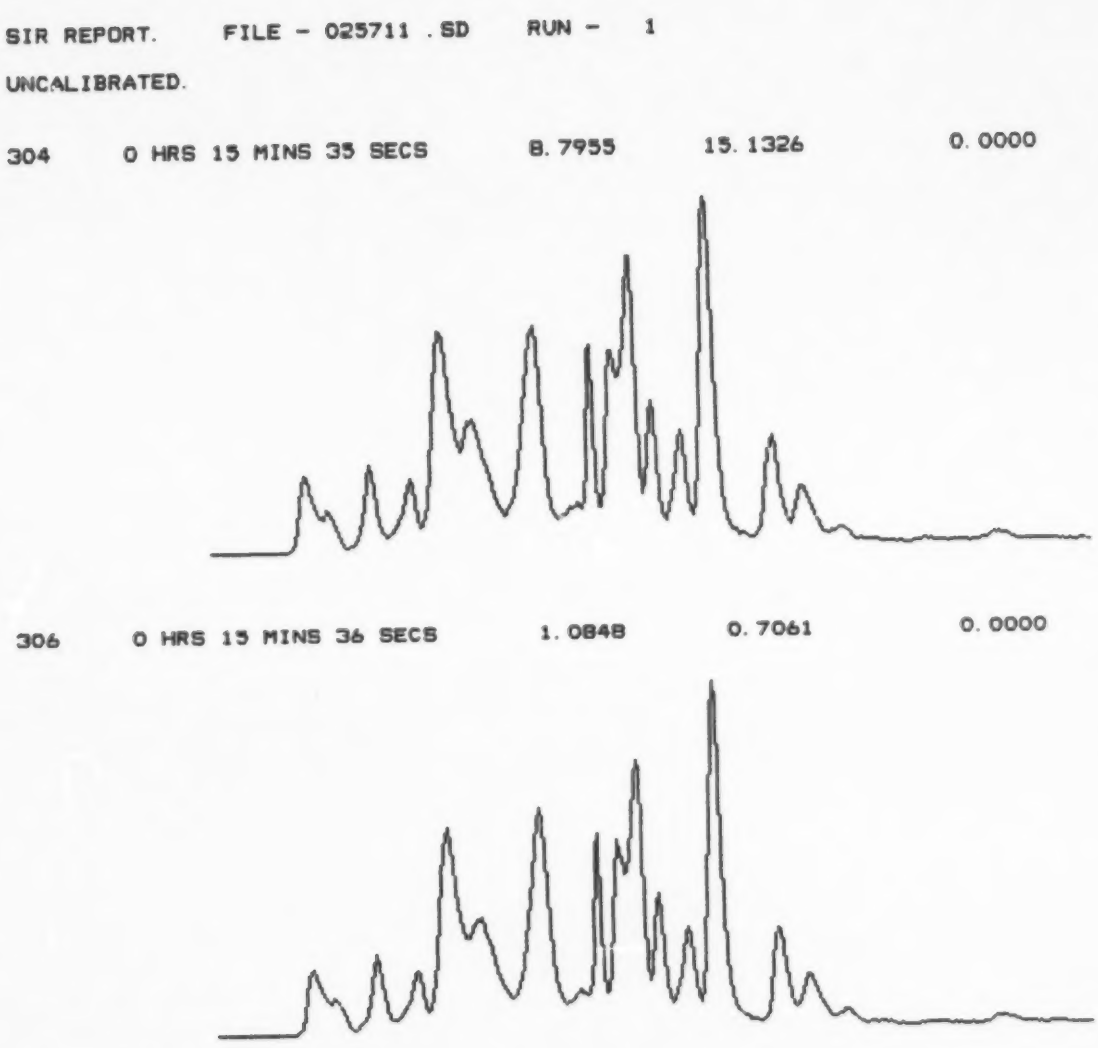

SIR REPORT. FILE - 025711 .SD RUN - 1
UNCALIBRATED.
304 0 HRS 15 MINS 35 SECS 8.7955 15.1326 0.0000
306 0 HRS 15 MINS 36 SECS 1.0848 0.7061 0.0000
RDF Gas Phase Sample
Mod. Method 5 Test No. 2

Figure B-5. Typical selected ion current profile for TCDF.

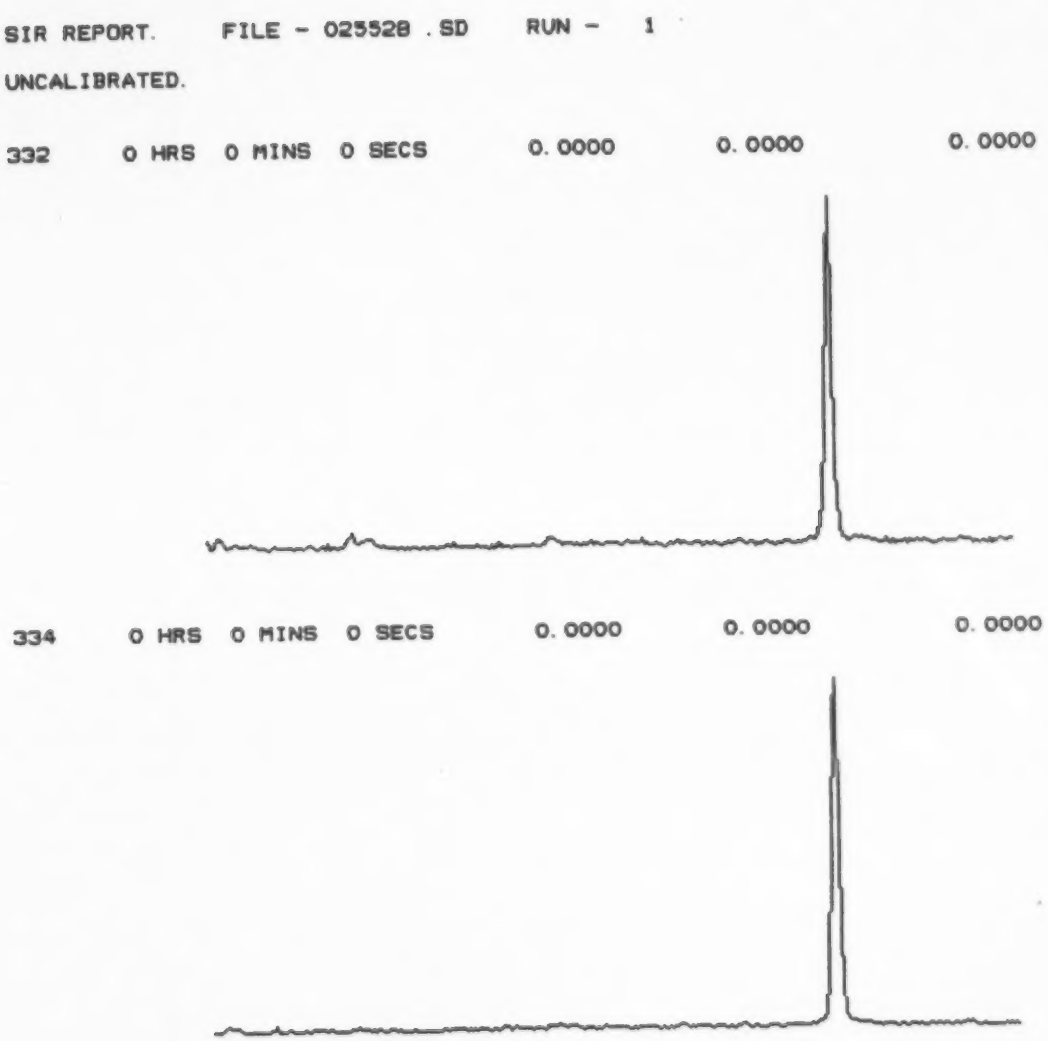
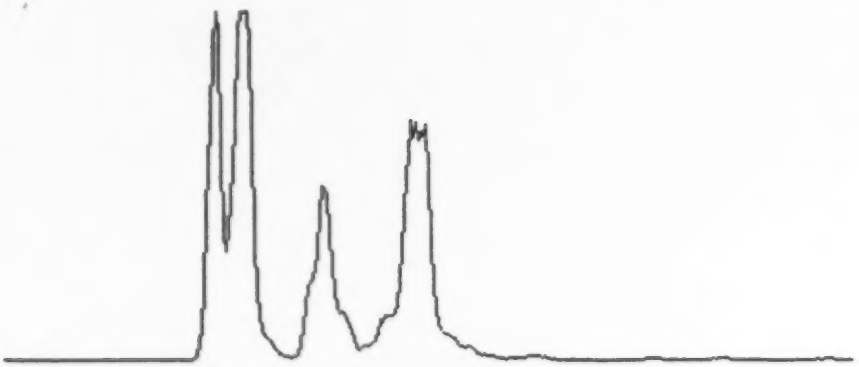

SIR REPORT. FILE - 025528 .SD RUN - 1
UNCALIBRATED.
332 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
334 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
RDF Gas Phase Sample
Mod. Method 5 Test No. 2

Figure B-6. Typical selected ion current profile for internal standard.

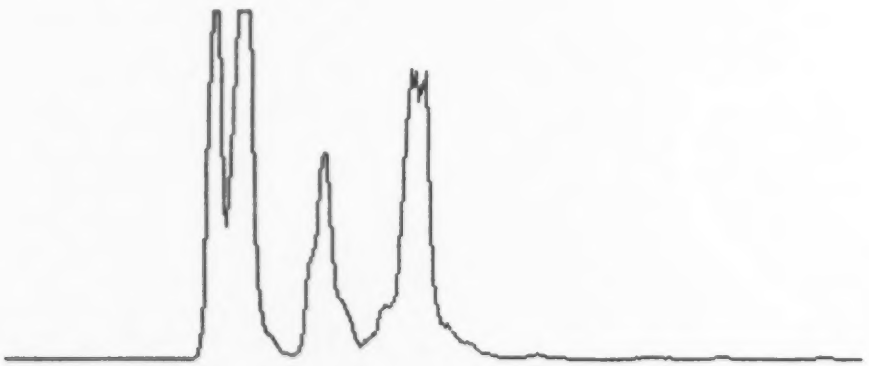
SIR REPORT. FILE - 093207 .SD RUN - 1

UNCALIBRATED.

320 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000



322 0 HRS 11 MINS 2 SECS 0.0000 0.0000 0.0000



MASS Particulate Sample
Mod. Method 5 Test No. 1

Figure B-7. Typical selected ion current profile for TCDD.

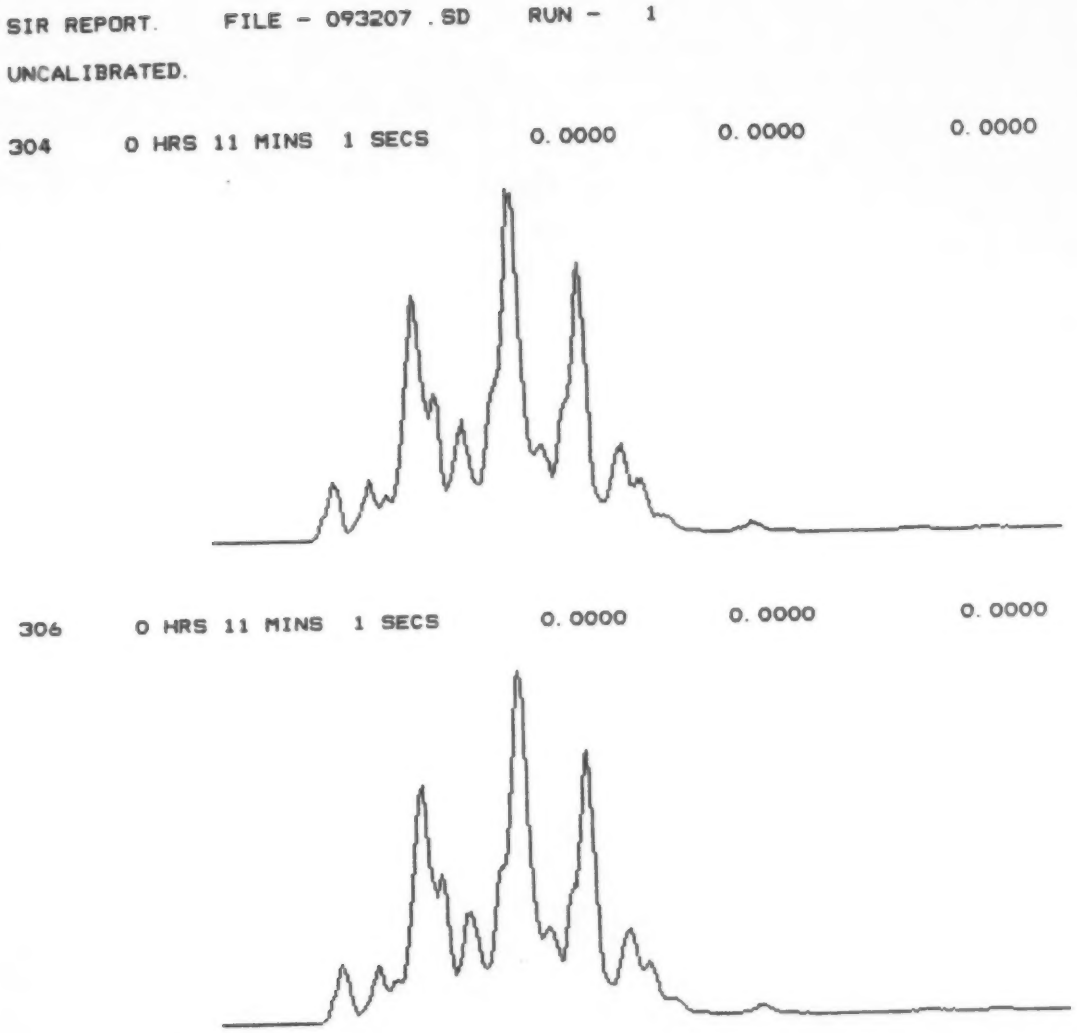

SIR REPORT. FILE - 093207 .SD RUN - 1
UNCALIBRATED.
304 0 HRS 11 MINS 1 SECS 0.0000 0.0000 0.0000
306 0 HRS 11 MINS 1 SECS 0.0000 0.0000 0.0000
MASS Particulate Sample
Mod. Method 5 Test No. 1

Figure B-8. Typical selected ion current profile for TCDF.

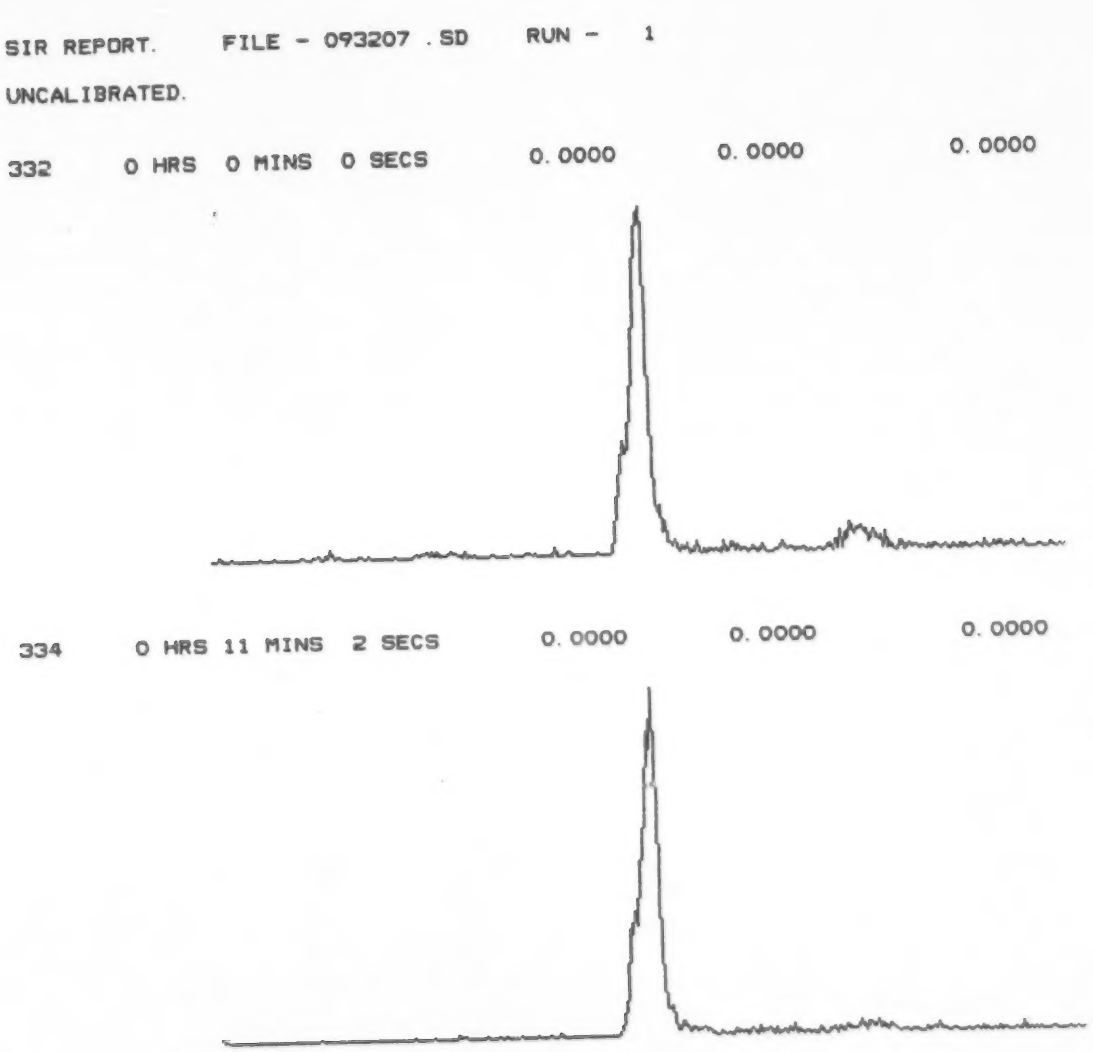
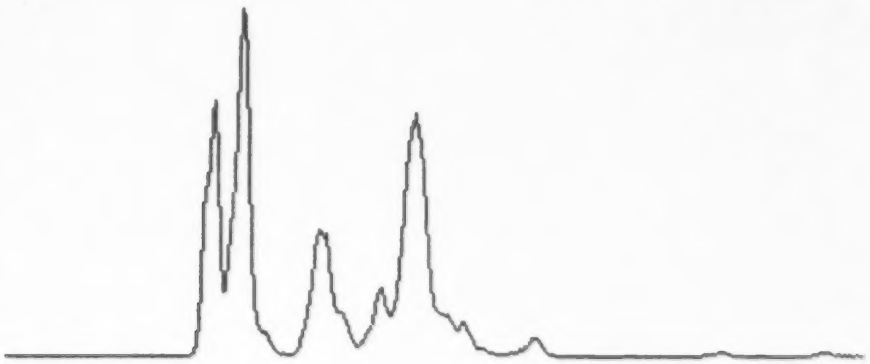

SIR REPORT. FILE - 093207 .SD RUN - 1
UNCALIBRATED.
332 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
334 0 HRS 11 MINS 2 SECS 0.0000 0.0000 0.0000
MASS Particulate Sample
Mod. Method 5 Test No. 1

Figure B-9. Typical selected ion current profile for internal standard.

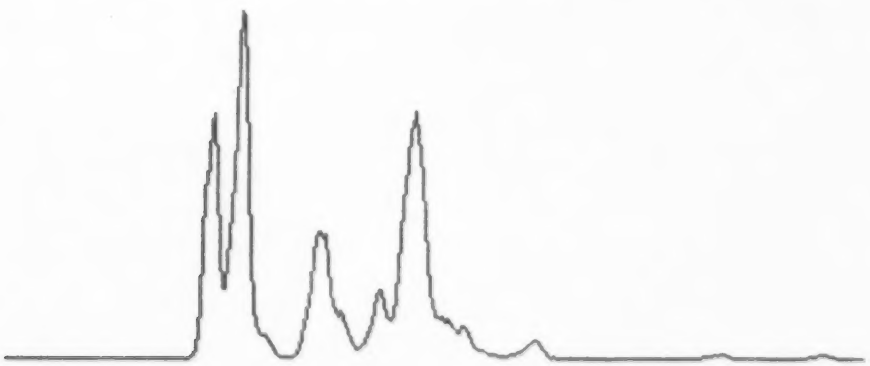
SIR REPORT. FILE - 093124 .SD RUN - 1

UNCALIBRATED.

320 0 HRS 11 MINS 1 SECS 0.0000 0.0000 0.0000



322 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000



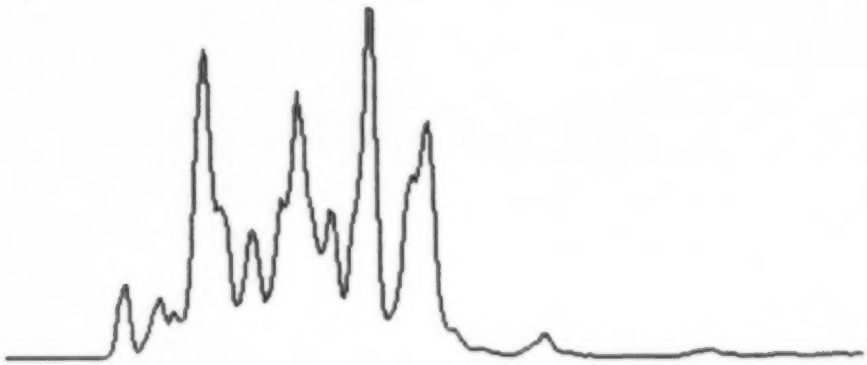
MASS Gas Phase Sample
Mod. Method 5 Test No. 1

Figure B-10. Typical selected ion current profile for TCDD.

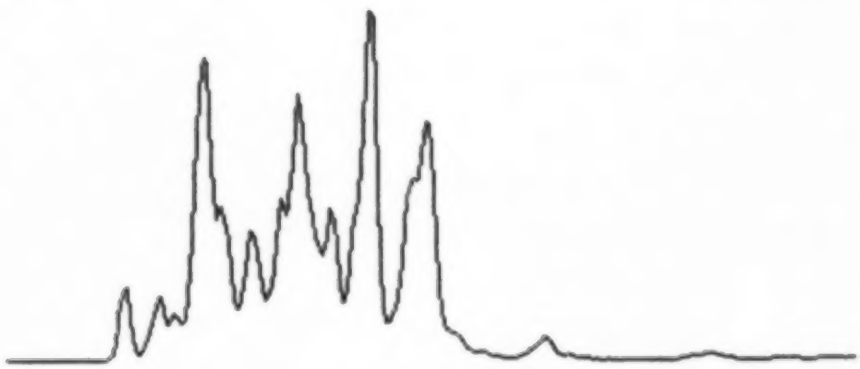
SIR REPORT. FILE - 093124 .SD RUN - 1

UNCALIBRATED.

304 0 HRS 11 MINS 1 SECS 0.0000 0.0000 0.0000



306 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000



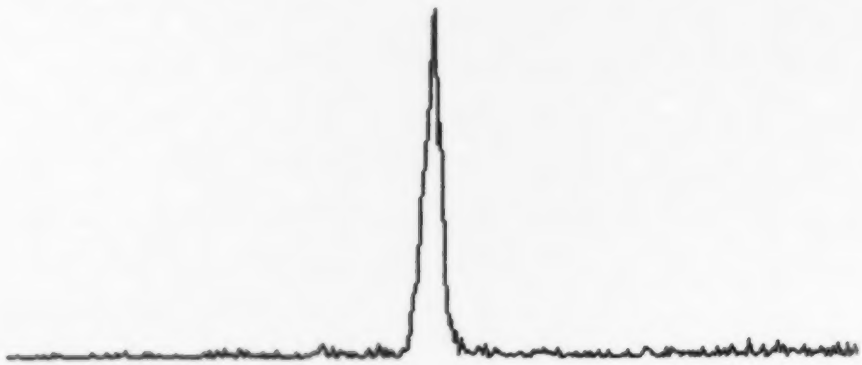
MASS Gas Phase Sample
Mod. Method 5 Test No. 1

Figure B-11. Typical selected ion current profile for TCDF.

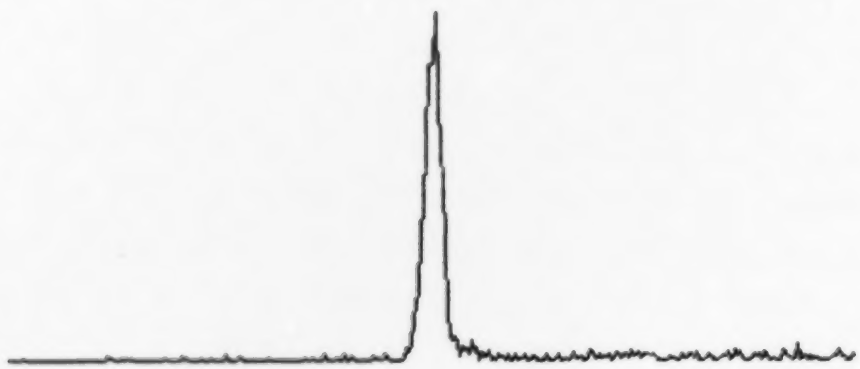
SIR REPORT. FILE - 093124 .SD RUN - 1

UNCALIBRATED.

332 0 HRS 11 MINS 2 SECS 0.0000 0.0000 0.0000



334 0 HRS 11 MINS 2 SECS 0.0000 0.0000 0.0000



MASS Gas Phase Sample
Mod. Method 5 Test No. 1

Figure B-12. Typical selected ion current profile for internal standard.

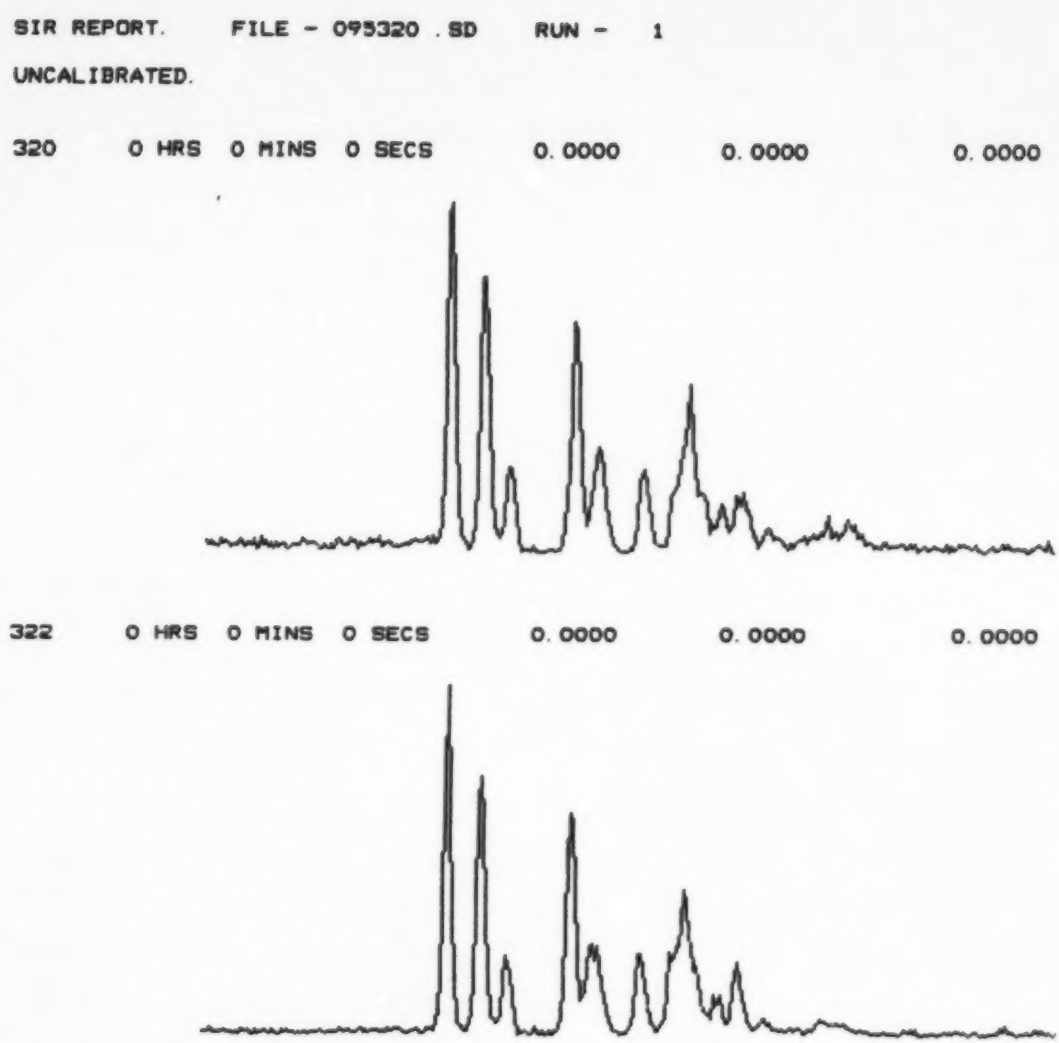

SIR REPORT. FILE - 095320 .SD RUN - 1
UNCALIBRATED.
320 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
322 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
MOD Particulate Sample
Mod. Method 5 Test No. 2

Figure B-13. Typical selected ion current profile for TCDD.

SIR REPORT. FILE - 095320 .SD RUN - 1

UNCALIBRATED.

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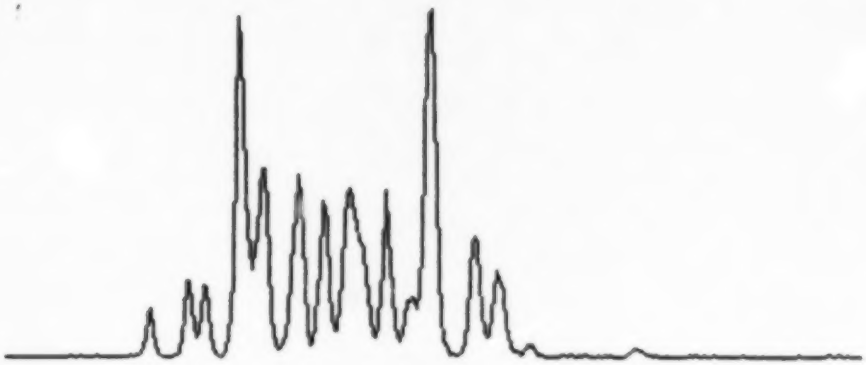
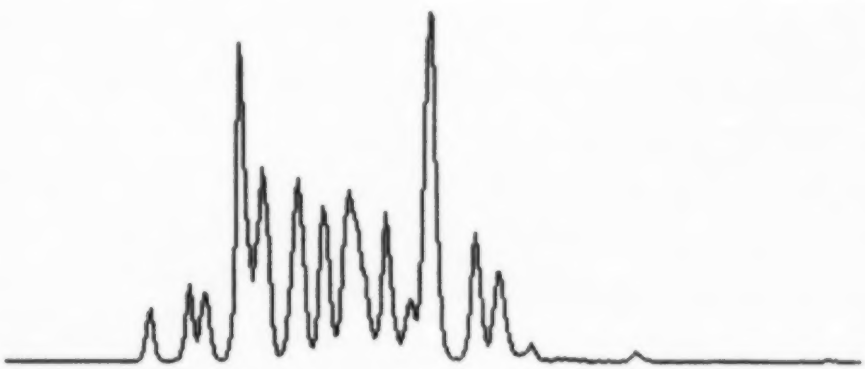


306 0 HRS 11 MINS 31 SECS 0.0000 0.0000 0.0000



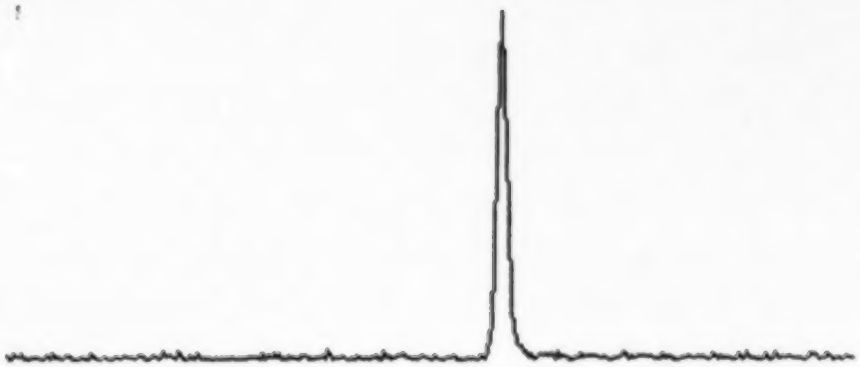
MOD Particulate Sample
Mod. Method 5 Test No. 2

Figure B-14. Typical selected ion current profile for TCDF.

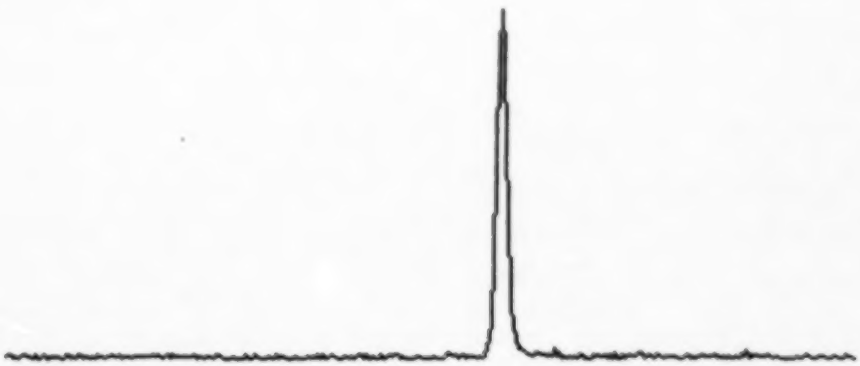
SIR REPORT. FILE - 095320 .SD RUN - 1

UNCALIBRATED.

332 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000



334 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000



MOD Particulate Sample
Mod. Method 5 Test No. 2

Figure B-15. Typical selected ion current profile for internal standard.

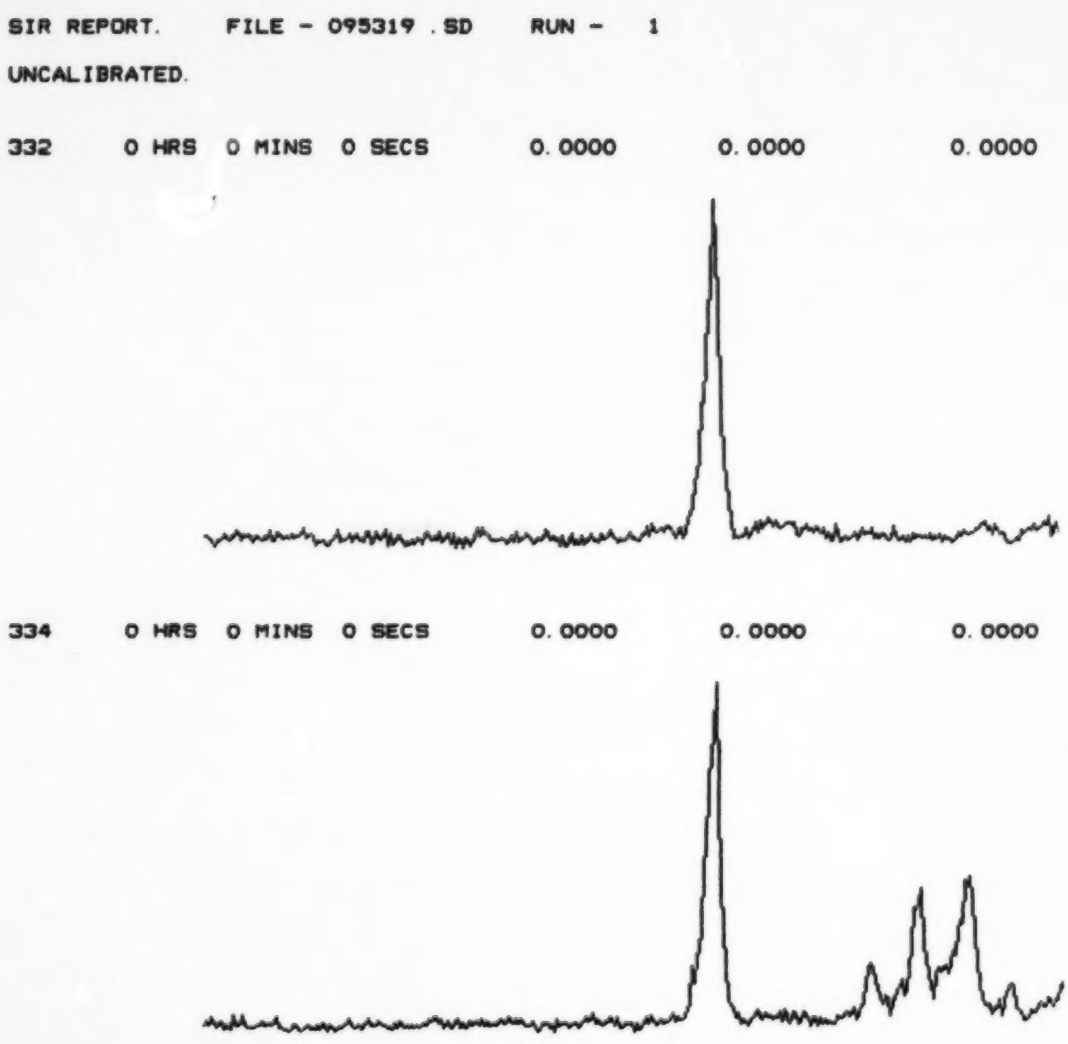
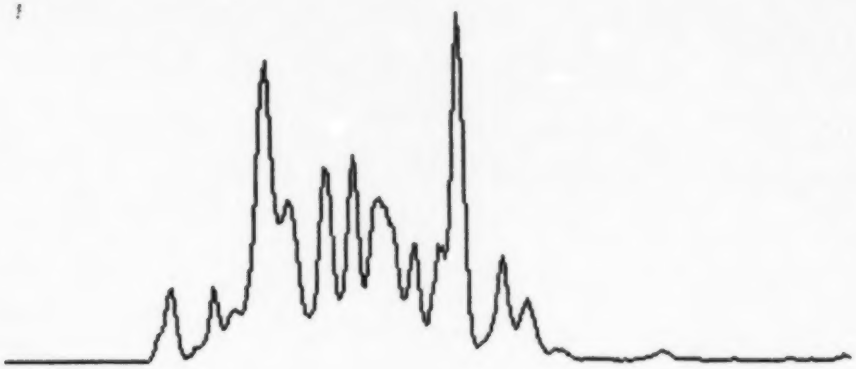

SIR REPORT. FILE - 095319 .SD RUN - 1
UNCALIBRATED.
332 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
334 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
MOD Gas Phase Sample
Mod. Method 5 Test No. 2

Figure B-16. Typical selected ion current profile for TCDD.

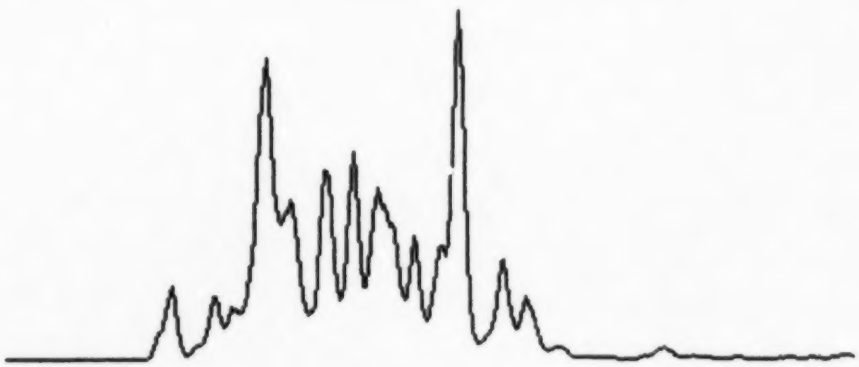
SIR REPORT. FILE - 095319 .SD RUN - 1

UNCALIBRATED.

304 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000



306 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000



MOD Gas Phase Sample
Mod. Method 5 Test No. 2

Figure B-17. Typical selected ion current profile for TCDF.

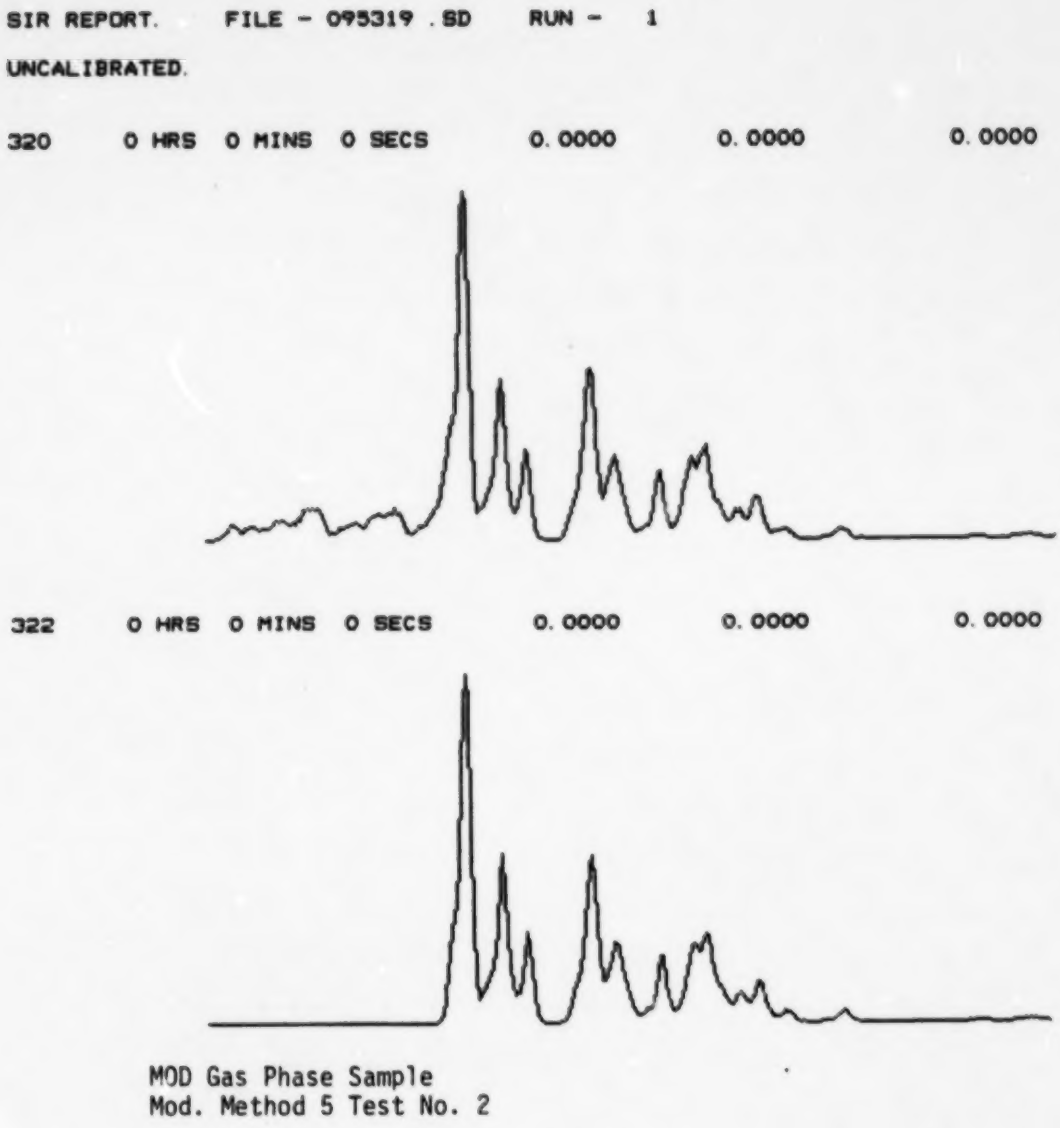

SIR REPORT. FILE - 095319 .SD RUN - 1
UNCALIBRATED.
320 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
322 0 HRS 0 MINS 0 SECS 0.0000 0.0000 0.0000
MOD Gas Phase Sample
Mod. Method 5 Test No. 2

Figure B-18. Typical selected ion current profile for internal standard.